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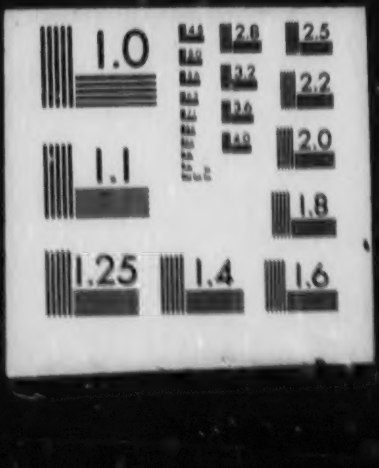
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PB-264 924

Environmental Assessment of Steelmaking Furnace Dust Disposal Methods

Research Triangle Inst, Research Triangle Park, N C

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, N C

Feb 77

PB 264 924

EPA-600/2-77-044
February 1977

Environmental Protection Technology Series

ENVIRONMENTAL ASSESSMENT OF STEELMAKING FURNACE DUST DISPOSAL METHODS

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

Industrial Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
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1. REPORT NO. EPA-600/2-77-044	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Environmental Assessment of Steelmaking Furnace Dust Disposal Methods		5. REPORT DATE February 1977 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) G.E. Weant III and M.R. Overcash		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Research Triangle Institute P.O. Box 12194 Research Triangle Park, NC 27709		10. PROGRAM ELEMENT NO. 1AB604 11. CONTRACT/GRANT NO. 68-02-1325, Task 61
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Task Final; 3-12/76 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer for this report is R.V. Hendriks, Mail Drop 62, 919/549-8411 Ext 2557.

16. ABSTRACT

The report gives results of a study to examine the nature of steelmaking furnace residues and disposal techniques, and to assess potential problems associated with residue disposal, a potential multimedia environmental problem. The study established a preliminary basis for impact evaluation. Solubilization tests of 18 furnace residue samples showed that the amount of metals extracted from the solids is a small percentage (less than 10 percent) of the total amount available in the residues, except for antimony and (in some cases) cobalt and zinc. Organic analysis of the solute showed low total organic carbon, except in four electric furnace samples. Further analysis of these four samples showed the types of products normally associated with the distillation of mineral- or petroleum-based lubricating oils. The study concludes that potential exists for environmental degradation from the disposal of these furnace residues. Due to variations in residue characteristics, climatic and topographic conditions, and disposal site configurations, a site by site investigation is necessary to further evaluate these environmental problems. The study also concludes that, although residue recycling is not economically feasible on a plant by plant basis, regional recycle plants can be operated profitably in some areas.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Residues	Pollution Control	13B
Iron and Steel Industry		Stationary Sources	11F
Steel Making	Disposal	Environmental Assessment	13H
Furnaces	Waste Disposal		13A
Dust	Circulation		11G
Dust Control	Lubricating Oils		11H

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 131
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE A07 - A01

EPA Form 2220-1 (9-73)

EPA-600/2-77-044
February 1977

ENVIRONMENTAL ASSESSMENT OF STEELMAKING FURNACE DUST DISPOSAL METHODS

by

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Contract No. 68-02-1325, Task 61
Program Element No. 1AB604

EPA Task Officer: Robert V. Hendriks

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

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ACKNOWLEDGMENTS

The authors wish to express their gratitude to a number of individuals for their help on various aspects of this report. Particular emphasis should be placed on the assistance received from Mr. William Benzer of AISI and environmental control officials from many steel companies in the U.S. for their help in acquiring residue samples for this study. Appreciation is also expressed to the various individuals who helped perform the residue analyses. These include Dr. R. M. Statnick and Mr. Hunter Dougherty of EPA, IERL/RTP and Dr. V. V. Cavaroc of NCSU's Department of Geosciences.

Special appreciation is extended to Dr. Philip Singer of UNC's Department of Environmental Sciences and Engineering for his help in the analysis of analytical data and Mr. Richard Jablin for his overall input of information.

SECTION 1

INTRODUCTION

Residues collected by air pollution control equipment on steelmaking furnaces is considered a potential multimedia environmental problem. This dust is frequently high in tramp metals and is not suitable for recycle. Thus, the residues are discarded, creating potential environmental problems as well as resulting in a waste of natural resources. Although recycling methods have been developed, they are presently in limited use for economic reasons.

The potential environmental problems associated with the residues result from its quantity (estimated to be approximately 1.9×10^9 kg in 1976), its fine particle size allowing wind erosion and entrainment, and the potential for water extraction of metals and organic materials leading to ground and surface water contamination. This report focuses on the potential of environmental contamination by characterizing the problem, examining handling and disposal problems, and by examining the residue and disposal characteristics that provide the potential for affecting the environment.

SECTION 2

CONCLUSIONS

A number of conclusions can be drawn from this study.

1. The potential exists for environmental degradation from the disposal of steelmaking furnace residues. There are many factors that influence this potential. These include particle size and shape, handling and disposal practices, wetness of disposed residues, type of disposal configuration, and climatological and topographical factors of each disposal site. The variation in these factors dictate a site-by-site investigation of environmental problems.
2. Generalizations of residue characteristics from a furnace type cannot be made. Even within a furnace type, residue characteristics have great variability. The residues show variations in particle size and shape, consistency, and chemical composition.
3. The steelmaking furnace sources of these residues are located in well defined areas of the U.S. Therefore, problems associated with residue disposal are generally localized.
4. A possibility exists for the profitable operation of regional recycling plants in several locations around the country, including Chicago and Pittsburgh and possibly Philadelphia and Dallas.
5. The disposal method plays an important part in producing the potential for adverse environmental effects. A trade-off can exist depending on the type of pollution to be avoided (i.e., air, surface runoff, or subsurface migration). The greatest potential for air emissions comes from piles and the least potential from lagoons and possibly landfills if they are covered by a soil layer. For runoff, the greatest potential comes from piles with impermeable bases and from filling gullies or natural depressions without dams; the least comes from landfills. For subsurface migration, the most potential comes from lagoons and gullies or natural depressions with dams with no overflows or drains, while the least comes from piles with impermeable bases and lined landfills. However, other factors such as topography and climate play an appreciable role.

SECTION 3

RECOMMENDATIONS

Adverse environmental impacts can result from the disposal of furnace dusts. A detailed study of residue disposal practices should be initiated based on the following steps:

1. A detailed assessment of the disposal steps with emphasis on gathering information in the field on the nature of the residues, wet and dry differences, configuration and nature of specific residue accumulations, drainage patterns, surface erosion, seepage patterns, etc.
2. Additional studies of the furnace residues including better definition of particle sizes; causes for pH changes in solutions (notably soluble iron and calcium); solubility tests using pH buffer systems; evaluation of secondary reactions in the water systems; evaluation of significant pathways into the environment by examining chemical compositions of solutes, changes in valence states, formation of colloids, and bonding to organic species; evaluation of particle emissions at each stage of the handling/disposal process; and leaching tests through soil columns.
3. Field monitoring of existing disposal sites to evaluate disposal site configurations as an influence on effluents.
4. Evaluation of control practices and alternatives.
5. Investigations of the fate of antimony, gallium, and germanium in soil-water-plant systems, since no information exists on their fate.

SECTION 4

CHARACTERIZATION OF THE PROBLEM

The disposal of residues collected by air pollution control equipment on steelmaking furnaces presents multimedia environmental problems because of both the quantity and the physical and chemical properties of the disposed waste. Approximately 62 percent of the residue is collected in dry form (from electrostatic precipitators and baghouses), while the remaining 38 percent is collected as a sludge from various types of wet scrubbers. The basic oxygen furnace accounts for about 80 percent of the sludge produced and the open hearth furnace for the remaining 20 percent. Sludge from electric furnaces is essentially negligible.[1]

The problems involved with the disposal of steelmaking residues are characterized by examining the sources, quantities, and characteristics of these residues.

4.1 SOURCES OF RESIDUE

Basically, three types of furnaces are used in the steelmaking process: open hearth, electric, and basic oxygen. The geographical distribution of these furnaces is shown in Figures 1 through 3.* Each mark designates the location of a steel facility with at least one furnace of the type represented by the figure.

4.2 QUANTITIES OF RESIDUE

Estimations of the total quantities of residues generated by steelmaking furnaces are hampered by variations in the reported data on both the quantities produced and quantities recycled and by the lag time associated with the publishing of steel production data--the latest data are from 1974.[3] The reported quantities (in kilograms of residue per 1000 kg of steel produced) vary from 11 to 20, 5.5 to 14, and 11 to 21 for open hearth, electric, and basic oxygen

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*Produced from information extracted from the Directory of Iron and Steel Works of the United States and Canada, 1974.[2]

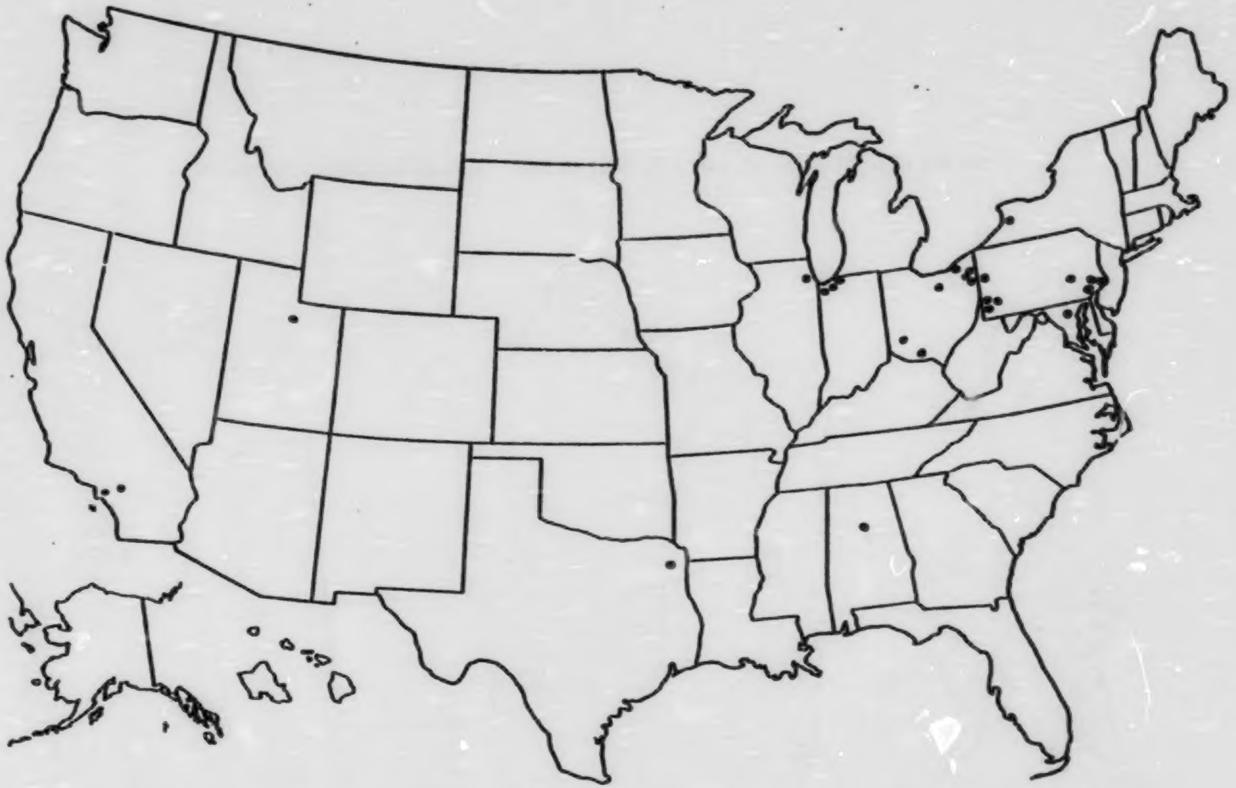

Figure 1. Geographical distribution of open hearth furnaces.

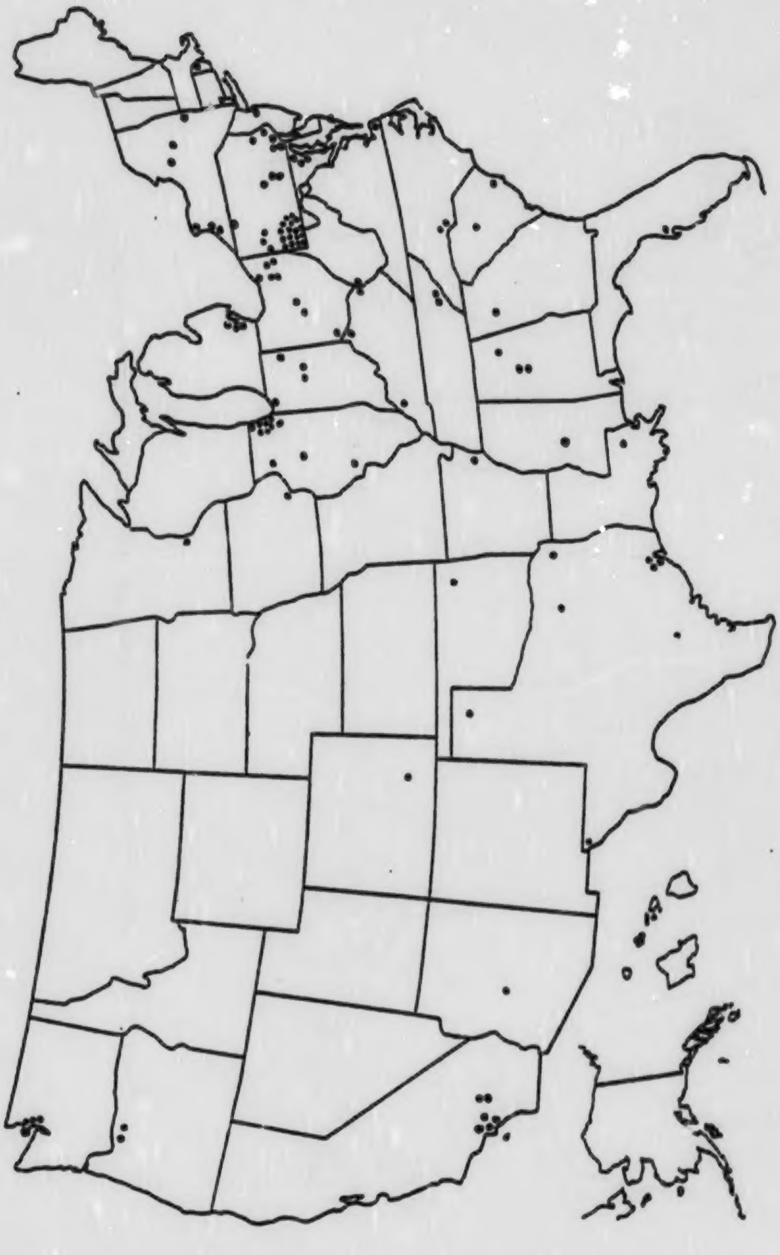

Figure 2. Geographical distribution of electric furnaces.

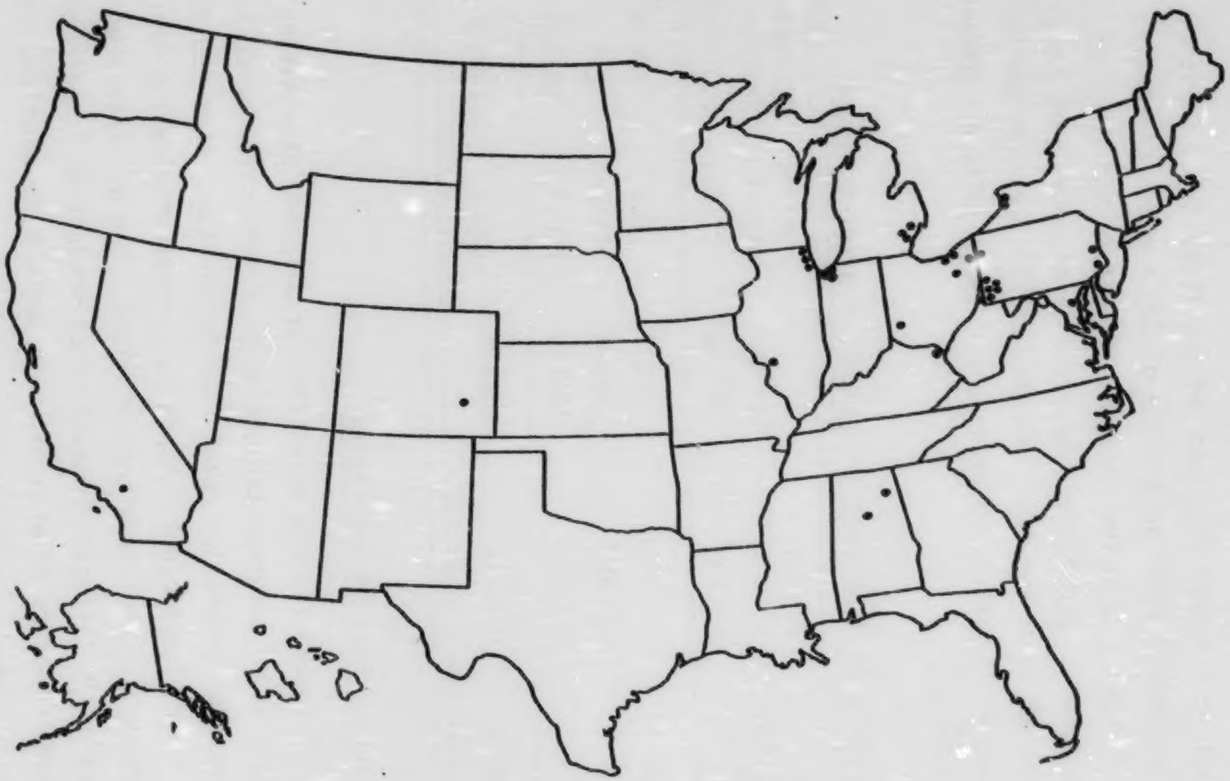

Figure 3. Geographical distribution of basic oxygen furnaces.

furnaces, respectively. The quantities recycled vary from 3 to 6 percent for electric furnaces and 15 to 25 percent for oxygen furnaces. The quantity recycled from open hearth furnaces is considered to be negligible.[1,4,5,6]

4.2.1 Estimation of 1974 Residue Generation

Residue generation for 1974 from each of the three types of steelmaking furnaces was estimated using an average of the residue generation factors (kg/1000 kg of steel) from the reported literature and the 1974 steel production statistics. Quantities subjected to disposal were then calculated using disposal percentages of 100, 95, and 80 for open hearth, electric, and basic oxygen furnaces, respectively. The results are presented in Table 1.

TABLE 1. ESTIMATION OF 1974 STEELMAKING FURNACE RESIDUES

Furnace Type	Steel Production (10^9 kg)	Residue Generation (kg/1000 kg)	Residue (10^6 kg)	Quantity Recycled (10^6 kg)	Disposed Residue (10^6 kg)
Open Hearth	32.2	14.5	466.9	0.0	466.9
Electric	26.0	10.5	273.0	13.7	259.3
Basic Oxygen	74.0	18.0	1332.0	266.4	1065.6
TOTAL	132.2	----	2071.9	280.1	1791.8

4.2.2 Estimation of Future Residue Quantities

The estimation of future residue quantities of disposed steelmaking furnace residues depends on an accurate projection of future steel production, the assumptions that residue generation rates will be constant, that new steelmaking technology will not significantly impact on current steelmaking practices, and that recycling methods will not be widely utilized. The accurate projection of future steel production is difficult because steel production is affected by a multitude of economic factors related to raw materials, production, and end uses. However, there seem to be few major developments that could significantly alter the current growth of the industry, and a simple linear projection of the current growth pattern should project future trends over the next decade with reasonable accuracy.

To accomplish this projection, a regression analysis was performed on total steel production from 1960 through 1974 (Figure 4). The scatter lines represent plus and minus 8.2 x 10^9 kg. The linear projection of this line through 1985 shows an annual growth rate of approximately 2 percent, a value consistent with demand estimates produced in one report.[7]

To meet the projected production in 1985 (165.7 x 10^9 kg), the steel industry must increase capacity. Since 1960, the capacity has grown at an average rate of 0.5 percent, well below the 2.0 percent growth in production.

The projection of steel production by furnace type involved the use of several assumptions. Basic oxygen furnaces are rapidly replacing the open hearths, causing a shift in the character of the industry in relation to scrap. The industry has become an overall scrap producer rather than a scrap consumer. This trend has been a major factor in the increased usage of the scrap consuming electric furnace.

Many steel companies have decided to keep their open hearth furnaces in order to maintain their scrap balance. This factor has resulted in a continual linear decline of the projection of steel production by open hearths for several years followed by a leveling of the trend line at about 2 percent of the total steel production.

The projection of open hearths at 2 percent of total production is justified by the projected steadily increasing production from electric furnaces, following many years of steady increases amounting to approximately 1 percent of total steel production per year. It is reasonable to assume that this pattern will continue.

Basic oxygen steelmaking was assumed to account for the remainder of the projected increased steel production. As the open hearth production levels out and the electric production remains on a steady increase, the basic oxygen production will slip slightly. These growth projections are shown in Figure 5.

Using these projections, residue generation rates, and the disposal percentages previously established, the estimates of disposed residue from 1974 to 1985 have been calculated and are shown in Table 2.

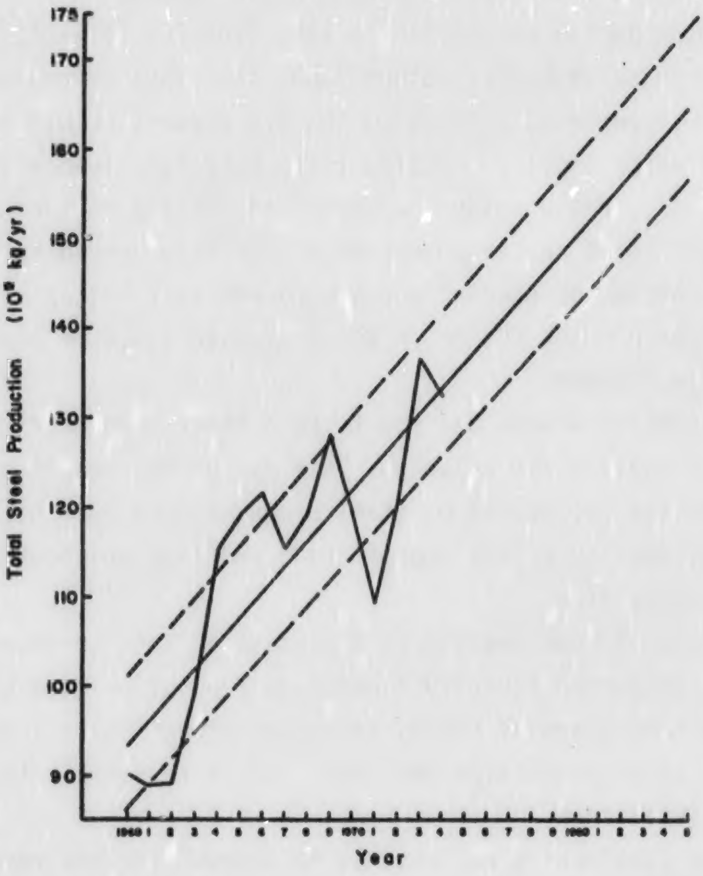

Figure 4. Total steel production projected through 1985.

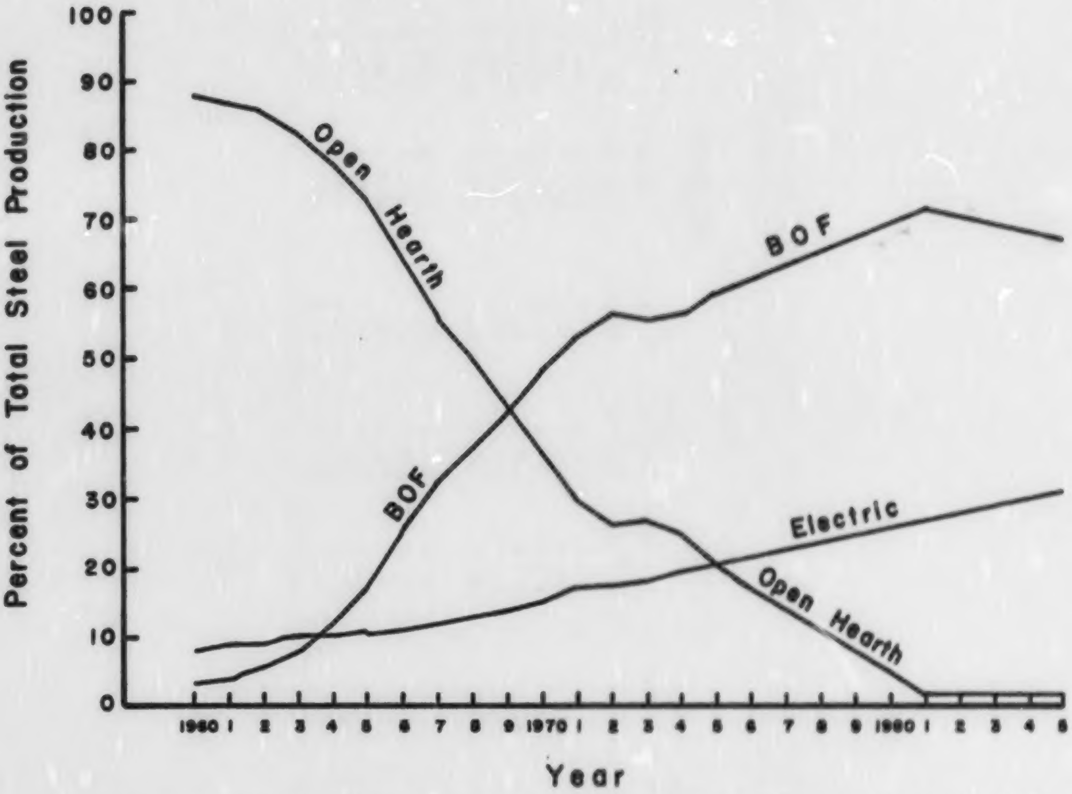

Figure 5. Steel production by furnace types projected through 1985.

TABLE 2. ESTIMATION OF STEEL PRODUCTION, RESIDUE GENERATION, AND DISPOSED RESIDUES FOR 1974 THROUGH 1985

	PROJECTED VALUES BY FURNACE TYPES											
	OPEN HEARTH			ELECTRIC			BASIC OXYGEN			TOTALS		
Year	Steel Production (10^9kg)	Residues (10^6kg)	Disposed Residues (10^6kg)	Steel Production (10^9kg)	Residues (10^6kg)	Disposed Residues (10^6kg)	Steel Production (10^9kg)	Residues (10^6kg)	Disposed Residues (10^6kg)	Steel Production (10^9kg)	Residues (10^6kg)	Disposed Residues (10^6kg)
1974	32.2	467.0	467.0	26.0	273.4	259.7	74.0	1332.5	1066.0	132.2	2073.0	1792.7
5	27.3	396.0	396.0	28.8	302.0	286.9	80.7	1451.7	1161.4	136.7	2149.7	1844.2
6	23.8	344.6	344.6	30.8	323.0	306.8	85.9	1533.3	1226.7	139.6	2201.0	1878.2
7	20.0	289.4	289.4	32.7	343.9	326.7	89.8	1616.6	1293.3	142.5	2250.0	1909.4
8	16.0	231.5	231.5	34.9	366.8	348.4	94.5	1701.5	1361.3	145.4	2299.8	1941.1
9	11.9	172.4	172.4	37.1	389.6	370.1	99.4	1789.7	1431.7	148.3	2351.7	1974.2
1980	7.5	109.2	109.2	39.3	412.5	391.8	104.3	1877.9	1502.3	151.2	2399.6	2003.4
1	3.1	44.7	44.7	41.6	437.3	415.4	109.3	1917.7	1574.2	154.0	2449.7	2034.3
2	3.1	44.7	44.7	43.9	461.0	438.0	110.2	1979.1	1583.3	156.9	2484.9	2066.1
3	3.1	44.7	44.7	46.7	490.6	466.0	110.4	1987.3	1589.9	159.8	2522.7	2100.6
4	3.1	44.7	44.7	48.8	512.5	486.9	110.9	1995.4	1596.4	162.8	2552.7	2128.0
5	3.1	44.7	44.7	51.3	539.1	512.2	111.2	2002.1	1601.6	165.7	2586.0	2158.5

4.3 RESIDUE CHARACTERIZATION

To characterize the residues from steelmaking furnace air pollution control equipment, residue samples were collected from 18 steel facilities around the Country. The furnace type, location, and type of pollution control equipment are presented in Table 3.

TABLE 3. FURNACE TYPE AND LOCATION AND POLLUTION CONTROL EQUIPMENT FOR 18 SAMPLES COLLECTED

Furnace Type	Sample Number	Furnace Location	Type of Pollution Control Equipment*
Open Hearth	1	Indiana	ESP
	2	California	ESP
	3	Ohio	ESP
	8	Ohio	ESP
	14	Ohio	WS
	17	Pennsylvania	ESP
Electric	4	Pennsylvania	BH
	5	Texas	BH
	6	Pennsylvania	BH
	7	Pennsylvania	BH
	12	Pennsylvania	BH
	13	Illinois	BH
	18	Ohio	ESP
Basic Oxygen	9	California	ESP
	10	Indiana	ESP
	11	Indiana	BH
	15	Ohio	WS
	16	Pennsylvania	ESP

*BH = Baghouse, ESP = Electrostatic Precipitator, WS = Wet Scrubber

These samples were analyzed to determine physical and chemical properties. Particle identification, size determinations, specific gravity determinations, and elemental analyses were performed. In addition, possible sources of elements in the occurring residue were investigated.

4.3.1 Particle Identification

Visual inspection, light micrsocopy, and electron microscopy were used both to characterize and to identify distinct particles in the dust samples. Each of the 18 samples was subjected to visual inspection and light microscopy while six arbitrarily chosen samples were examined by electron microscopy.

4.3.1.1 Visual Inspection and Light Microscopy--

Light microscopy observations were performed at 80X and 200X. These results are presented in Table 4. Terms describing particle size are relative to other samples only.

TABLE 4. RESULTS OF VISUAL INSPECTION AND LIGHT MICROSCOPY OF DUST SAMPLES

Sample Number	Color	Consistency and Description of Distinguishable Particles*
1	Rust Brown	Agglomerated rust brown particles and "faceted" spheres of pyritic-like particles
2	Rust Brown	Very fine agglomerated rust brown and pyritic-type particles--some separate irregular pyritic particles
3	Rust Brown	Agglomerated rust brown and separate irregular pyritic particles
4	Chocolate Brown	Extremely fine agglomerated brown particles--white calcium particles--small pyritic colored particles
5	Grayish Brown	Unagglomerated pyritic-like spheres with rust brown particles adherring, irregular pyritic masses--carbon flakes
6	Chocolate Brown	Agglomerated brown particles--pyritic-like particles occur as (1) irregular, angular to subangular, (2) shards, and (3) spheres
7	Rust Brown	Agglomerated rust brown particles--irregular, crystalline, white calcium particles with adherring red hematite particles--irregular and spherical pyritic particles--separate red hematite

continued

TABLE 4. (Cont'd)

Sample Number	Color	Consistency and Description of Distinguishable Particles*
8	Rust Brown	Agglomerated brown particles--some cubic pyrite
9	Chocolate Brown	Agglomerated brown particles--approximately 30 percent white calcium particles with adhering red hematite--irregular pyritic particles
10	Rust Brown	Agglomerated brown particles--white, crystalline calcium particles with adhering red hematite--irregular pyrite
11	Steel Gray	Agglomerated spherical particles
12	Chocolate Brown	Aggomerated brown particles--small amount of irregular, white calcium with adhering red hematite--large and small, irregular, spherical, and angular pyrite--small black chunks, possibly magnetite
13	Grayish Brown	Agglomerated, extremely fine particles--small, irregular and elongated pyritic particles--black, irregular, and spherical particles, probably magnetite
14	Chocolate to Rust Brown	Very fine agglomerated red brown and pyritic particles--gray particles, possibly carbon
15	Steel Gray	Extremely fine-grained agglomerated masses of gray pyritic-type particles--distinct particles not distinguishable at 200x
16	Chocolate Brown	Agglomerated red-brown particles--extremely large chunks of flaky material with color of pyrite but form of carbon--crystalline, white calcium with adhering red hematite--small irregular pyrite--black, spherical particles, possibly magnetite
17	Rust Brown	Agglomerated rust brown particles, extremely fine-grained--small pyritic particles embedded in agglomerated masses--small, embedded black particles, possibly magnetite
18	Chocolate Brown	Very fine agglomerated rust colored particles--white calcium and gold pyritic particles in agglomerated masses

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*Terms describing particle size are relative to other samples only.

4.3.1.2 Electron Microscopy--

Two samples from each of the three types of furnaces were examined by electron microscopy and associated X-ray diffraction analysis.

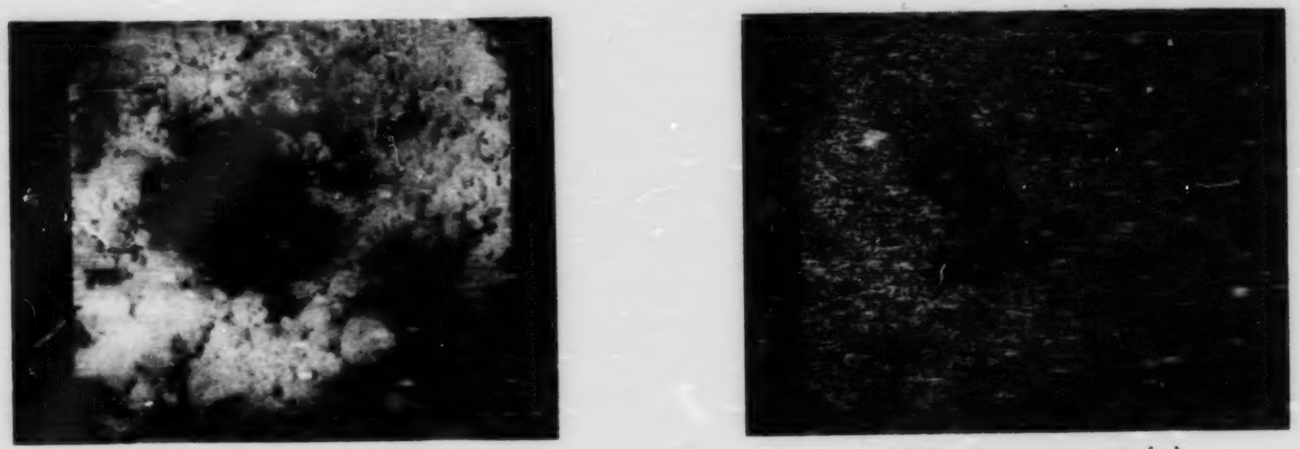
4.3.1.2.1 Open Hearth Furnace Samples -- Both open hearth furnace samples were chiefly composed of agglomerated, spherical iron particles. In addition, Sample No. 2 contained irregular carbon flakes, while Sample No. 14 contained irregular calcium particles. X-ray analysis showed that Sample No. 2 was composed of several elements not found in Sample No. 14. These included Mg, Si, P, Cl, and Cu. Table 5 summarizes the characteristics of the two samples.

TABLE 5. SUMMARY OF OPEN HEARTH FURNACE PARTICLE CHARACTERISTICS

Characteristic	Sample No. 2	Sample No. 14
Consistency	Agglomerated masses of iron spheres, irregular carbon flakes	Agglomerated masses of Fe/S spheres, large, irregular Ca/S particles
X-ray Analysis	Mg (trace), Si, P (trace), S, Cl, K, Ca, Cr (trace), Mn, Fe, Cu (trace), and Zn (trace)	S, K (trace), Ca, Cr (trace), Mn, Fe, and Zn
Particle Size Range	Iron--up to 2.3 μm Carbon--up to 183 μm	Iron--0.4 - 0.75 μm Calcium--0.56 - 5.6 μm

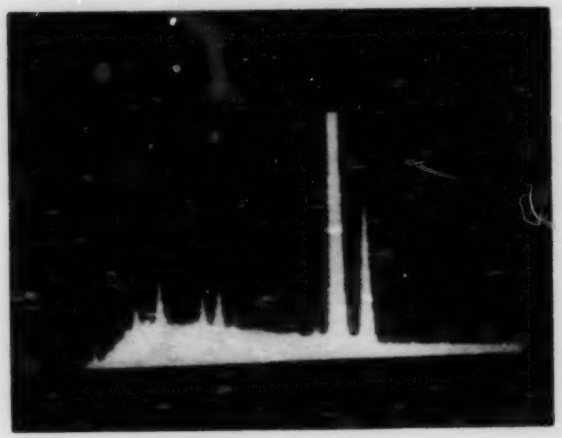
The No. 2 Sample--Figure 6a is a 153X photograph of the agglomerated sample with a carbon flake in the center, 6b is an iron map of the area that clearly outlines the carbon flake, and 6c is an X-ray spectrum of the sample.

Further examination of the particle in the center of the photo showed a flaky carbon particle with agglomerated iron particles adherring to its surface as shown in Figure 7a. An X-ray spectrum of this particle is shown in 7b, revealing the presence of chlorine and iron. The iron signal comes from both the surrounding and the adhering iron particles. Figure 7c is chlorine map, showing the dispersed nature of the chlorine and suggesting that the chlorine has been adsorbed by carbon.



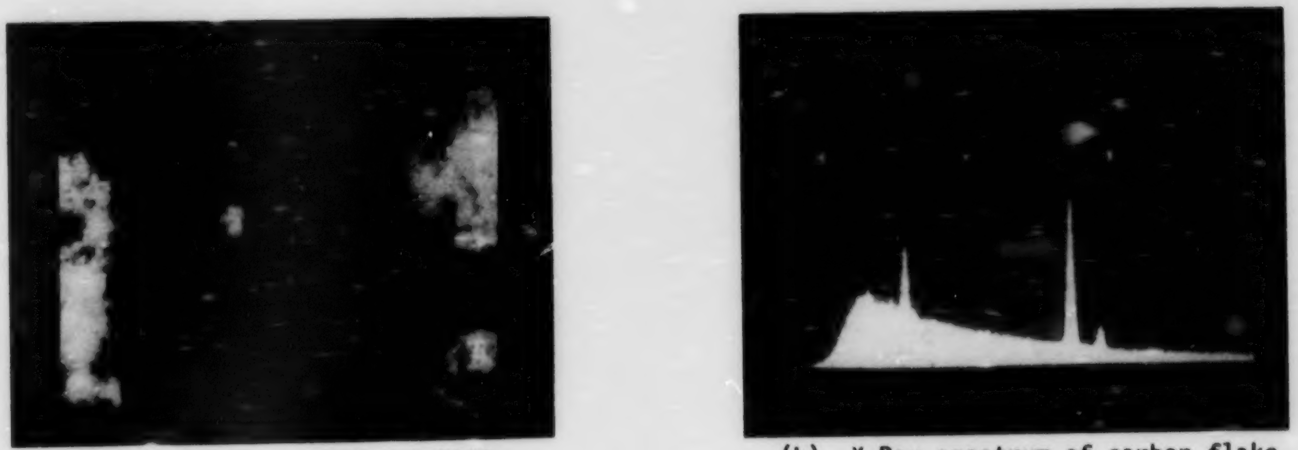
(a) Photo of sample at 153x.

(b) Iron map of (a).



(c) X-Ray spectrum of the sample showing Si, P (trace), S, K, Ca, Cr (trace), Mn, Fe, Cu (trace), and Zn (trace).

Figure 6. Examination of the No. 2 open hearth furnace sample.



(a) Photo of carbon flake at 2200x.

(b) X-Ray spectrum of carbon flake.

(c) Chlorine map of carbon particle.

Figure 7. Examination of the carbon flakes in the No. 2 open hearth sample.

The No. 14 Sample -- This sample is composed of agglomerated masses of spherical iron and irregular iron and calcium particles as shown in Figure 8a. The results of iron, calcium, and sulfur mappings are shown in Figures 8b, 8c, and 8d respectively. The sulfur mapping was made possible because of the high amount of sulfur in the sample (Figure 9b). The maps distinguish between iron and calcium particles and also indicate that the iron and calcium occur as sulfur compounds.

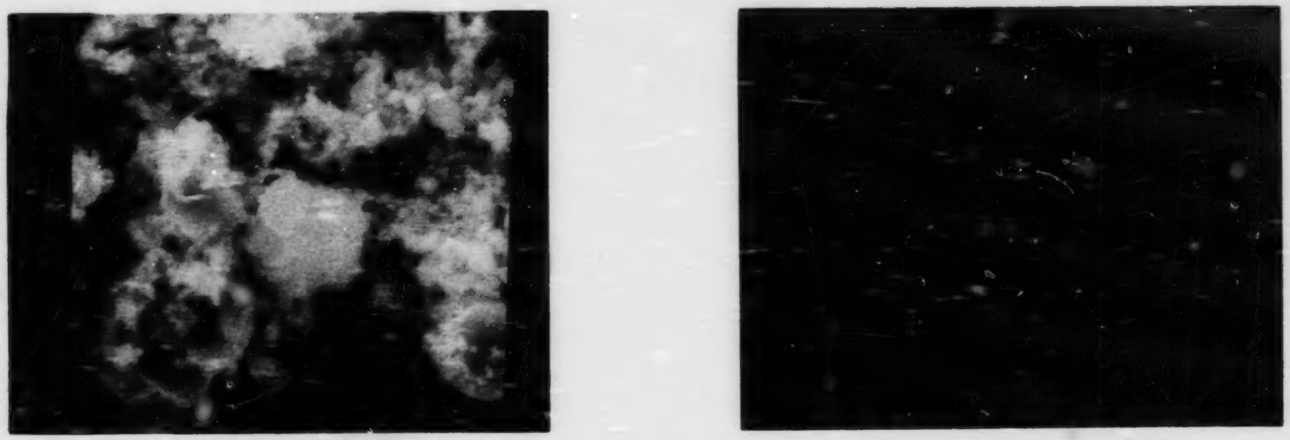
Figure 9 shows the sample at 13,500X and an X-ray spectrum of the sample. Particle sizes in this sample range from 0.04 to 0.75 μm.

4.3.1.2.2 Electric Furnace Samples -- The two electric furnace samples differed markedly, with the No. 5 sample showing distinct, unagglomerated particles and the No. 18 showing agglomerated masses. The No. 5 sample contained cubes of titanium, irregular carbon particles, and irregular, but well-rounded iron particles in addition to the spherical iron particles and irregular calcium particles shown by both of the samples.

Other differences include the particle size ranges and the occurrence of phosphorous, titanium, and chromium in the X-ray analysis of the No. 5 sample. The X-ray analysis also showed a much stronger calcium peak. A summary of the characteristics of these two samples is shown in Table 6.

TABLE 6. CHARACTERISTICS OF ELECTRIC FURNACE SAMPLES

Characteristic	Sample No. 18	Sample No. 5
Consistency	Agglomerated masses of spherical iron and irregular calcium particles	Unagglomerated spherical iron; rounded, irregular iron; irregular, sub-angular to subrounded calcium; irregular carbon; and cubic titanium particles
Particle Size	Iron--0.06 - 2.08 μm Calcium--0.5 - 1.0 μm	Iron--0.04 - 62.09 μm Calcium--0.28 - 37.93 μm (longest length) Carbon--up to 900 μm (longest length) Titanium--3.5 - 13.9 μm
X-Ray Analysis	Mg (trace), Si, S, Cl, K, Ca, Mn, Fe, Zn	Mg (trace), Si (trace), P (trace), S, Cl, K, Ca, Ti, Cr, Mn, Fe, Zn



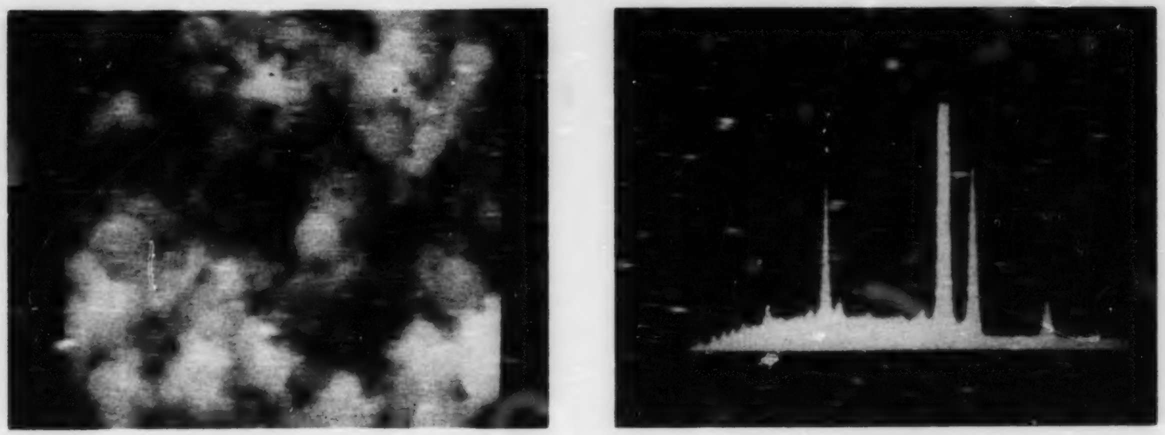
(a) Photo of sample at 4500x.

(b) Iron map of sample.

(c) Calcium map of sample.

(d) Sulfur map of sample.

Figure 8. Electron microscopy investigation of the No. 14 open hearth furnace sample.



(a) Photo of sample at 13,500x.

(b) X-Ray spectrum of sample showing S, K (trace), Ca, Cr (trace), Mn, Fe, and Zn.

Figure 9. Further characterization of the No. 14 open hearth furnace sample.

The No. 18 Sample -- This sample is composed of agglomerated masses of spherical iron and irregular calcium particles in approximate percentages of 92 and 2. Figure 10 shows two magnifications and an X-ray of the sample.

The No. 5 Sample -- This sample is composed of unagglomerated particles. However, adherence of smaller particles to larger ones is commonplace in this sample. The sample (Figure 11) is composed of both spherical and irregular but rounded particles composed of iron with much smaller calcium and iron particles adhering, carbon flakes with titanium, and separate irregular calcium particles.

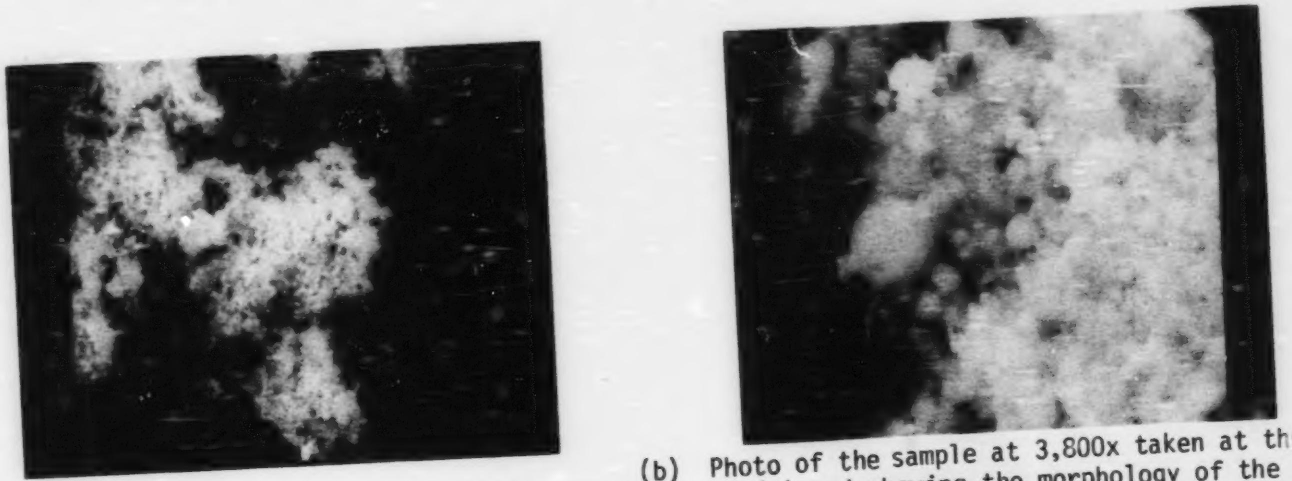
Further examination of the spherical particles shown in Figure 11a led to the assumption that these were iron spheres with irregular calcium particles adhering to their surface. The result of this examination is shown in Figure 12.

Figure 12a shows four spherical particles located in the bottom left corner of Figure 11a. Each sphere shows adhering particles with the center sphere showing larger adhering particles. Figure 12b is an iron map of the particles while Figure 12c is a calcium map. In 12c, the calcium shows up much stronger for the center particles. This is probably a result of the larger adhering particles that are most likely calcium. The conclusion drawn from this examination is that the spheres are most likely iron with adhering calcium particles.

Further examination of a carbon flake in Sample No. 5 revealed the adhesion of spherical iron, irregular calcium, and cubic titanium particles. Figure 13 shows the first step in the examination process taken at 450X. Figure 13a shows the surface of the carbon flake and the adhering particles, 13b is an iron map of this surface (the locations of iron are scattered and not concentrated), and 13c is a calcium map showing the same scattering as b. Figure 13d is a titanium map showing the concentration of titanium in areas occupied by cubic particles as shown in 13a. The cubic titanium particles range in size from 3.5 to 13.9 μm.

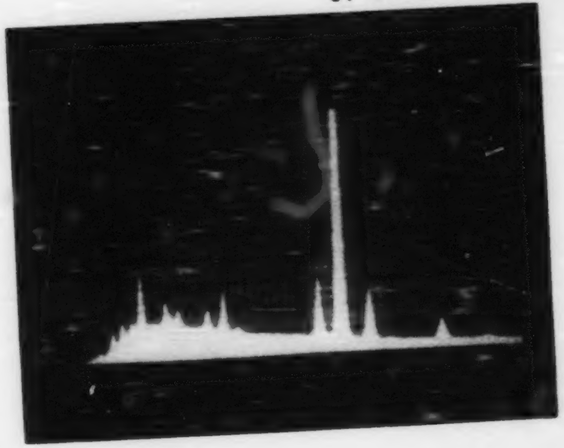
Figure 14 is a titanium cube at 6000X. This particle is a 7.4 μm cube.

Figure 15 gives the results from a further examination of the carbon flake at 9000X. In 15a, spherical and irregular particles adhering to the carbon flake are shown, 15b is an iron map showing a distinct iron concentration where the adhered particles lie, and 15c, the calcium map, also shows a



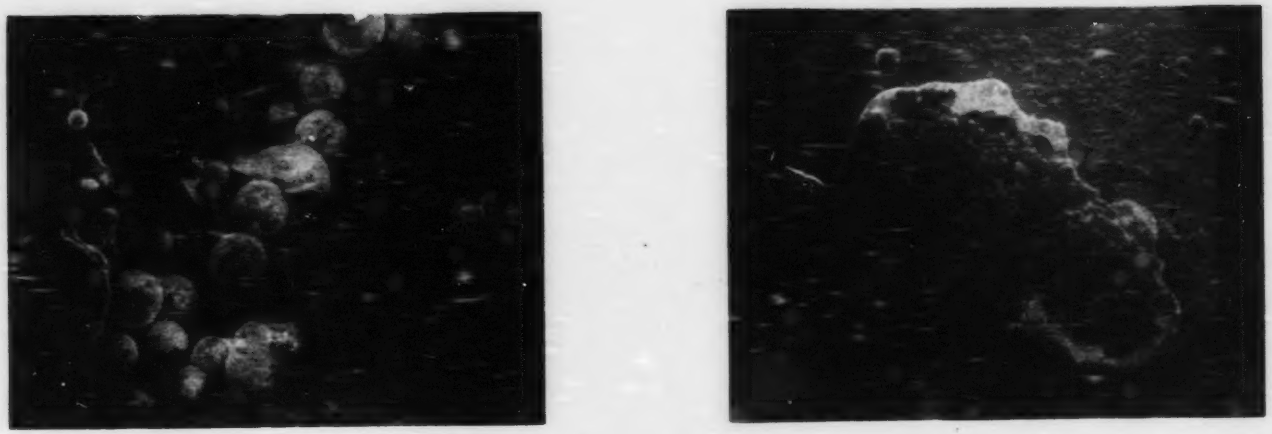
(a) Photo of the sample at 450x showing agglomerated masses.

(b) Photo of the sample at 3,800x taken at the center of (a) and showing the morphology of the agglomerated particles. Distinct particles are in the size range of 0.06 to 2.08 μ.



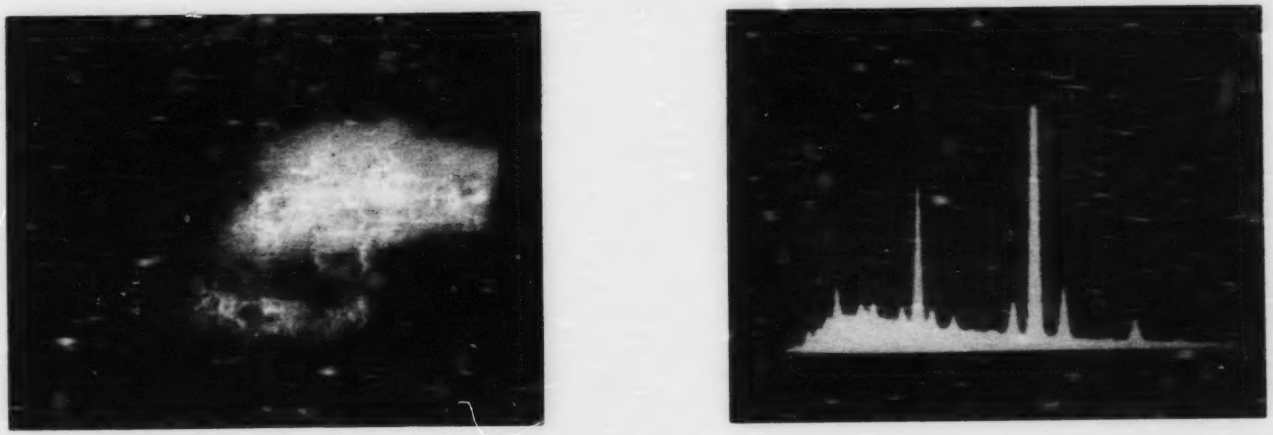
(c) X-Ray of the sample showing Mg (trace), Si, S, Cl, K, Ca, Mn, Fe, and Zn.

Figure 10. Electron microscopy of the No. 18 electric furnace sample.



(a) Photo of spherical and irregular, well rounded iron particles at 225x. Shows small particle adherence to larger ones. Largest spheres are approximately 62 μ in diameter.

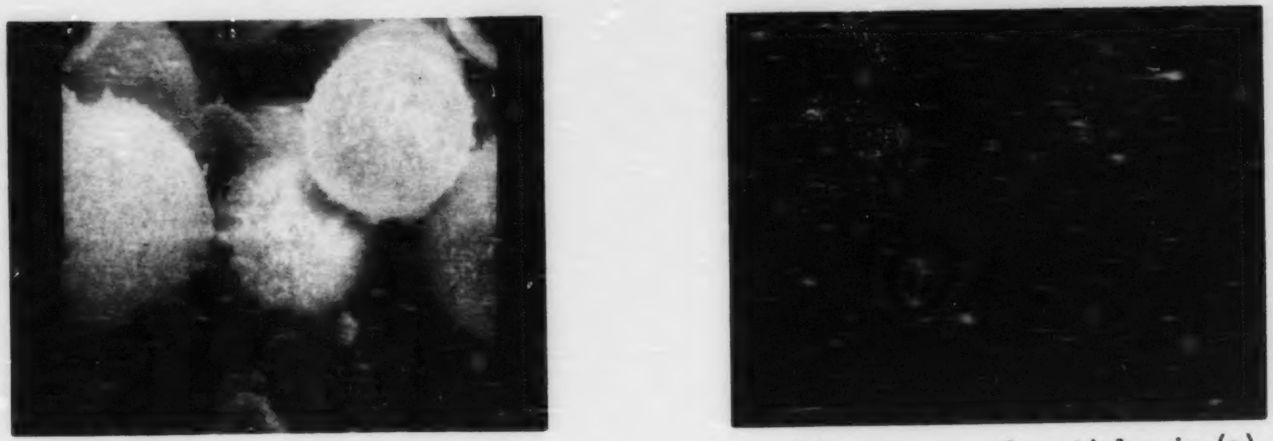
(b) Photo of irregular carbon particle at 90x. Particle is approximately 900 μ at largest length.



(c) Photo of irregular calcium particle at 2250x. Particle is approximately 38 μ at longest length

(d) X-Ray spectrum of sample showing Mg (trace), Si (trace), P (trace), S, Cl, K, Ca, Ti, Cr (trace), Mn, Fe, and Zn.

Figure 11. Electron micrographs and X-Ray of the No. 5 electric furnace sample.

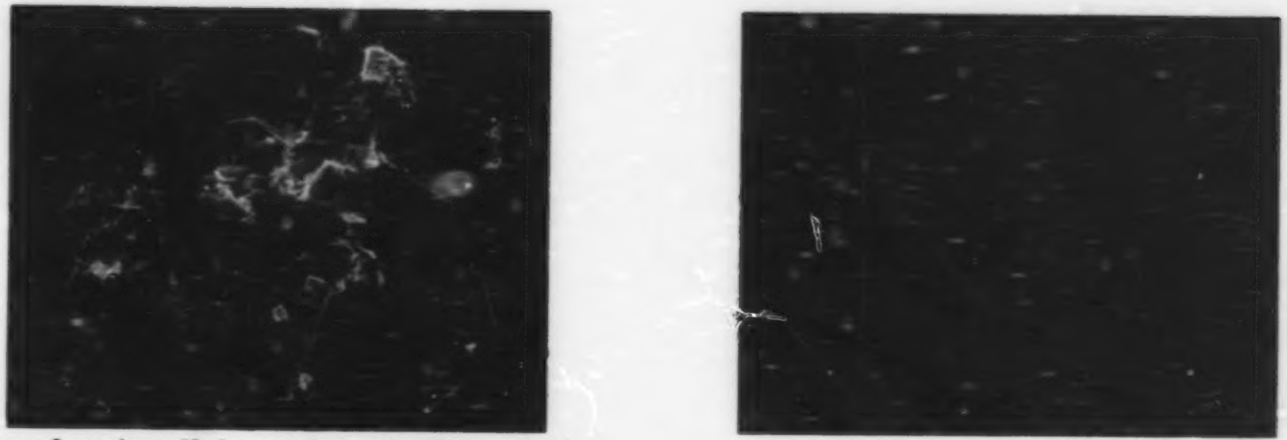


(a) Photo of spheres at 900x.
Shows irregular adhering particles.

(b) Iron map of particles in (a).

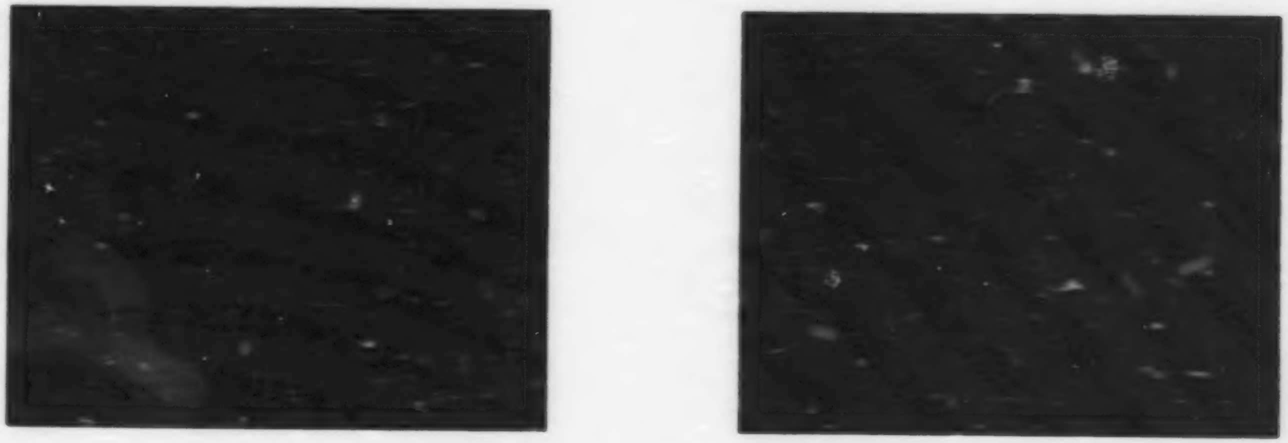
(c) Calcium map of particles in (a).

Figure 12. Results of the examination of the spherical particles in the No. 5 electric furnace sample.



(a) Photo of carbon flake surface at 450x. Notice cubic titanium, and scattered spherical and irregular particles adhering to the surface.

(b) Iron map of (a).



(c) Calcium map of (a).

(d) Titanium map of (a).

Figure 13. Examination of carbon flake at 450x.

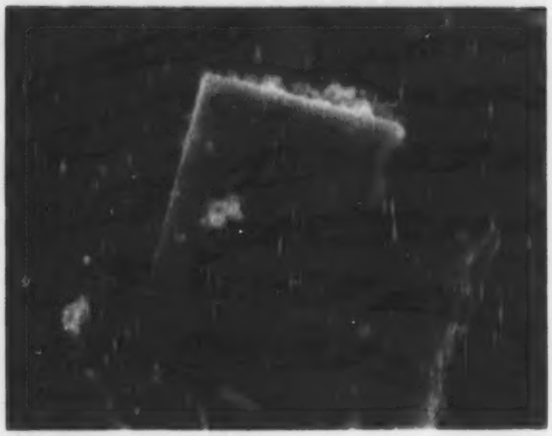
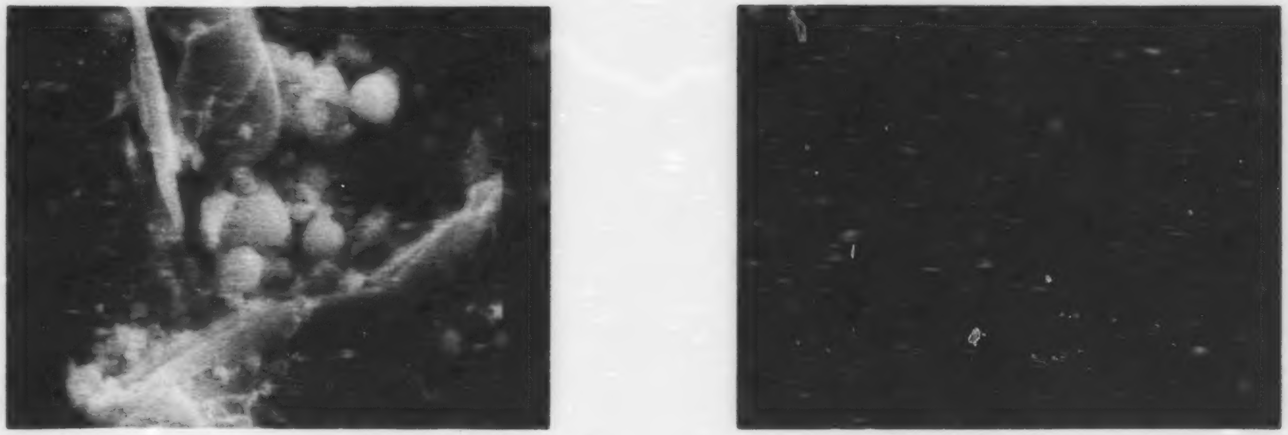
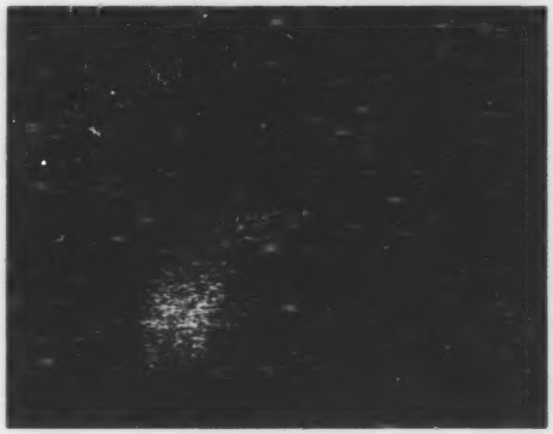


Figure 14. Titanium cube at 6000x.



(a) Photo of carbon flake and ahering particles at 9000x. Distinguishable particles range in size from 0.4 to 1.06 μ.

(b) Iron map.



(c) Calcium map.

Figure 15. Examination of carbon flake in sample No. 5 at 9000x.

distinct concentration of calcium in the areas of the adhered particles. With the aid of these maps, iron and calcium particles can be distinguished in some cases.

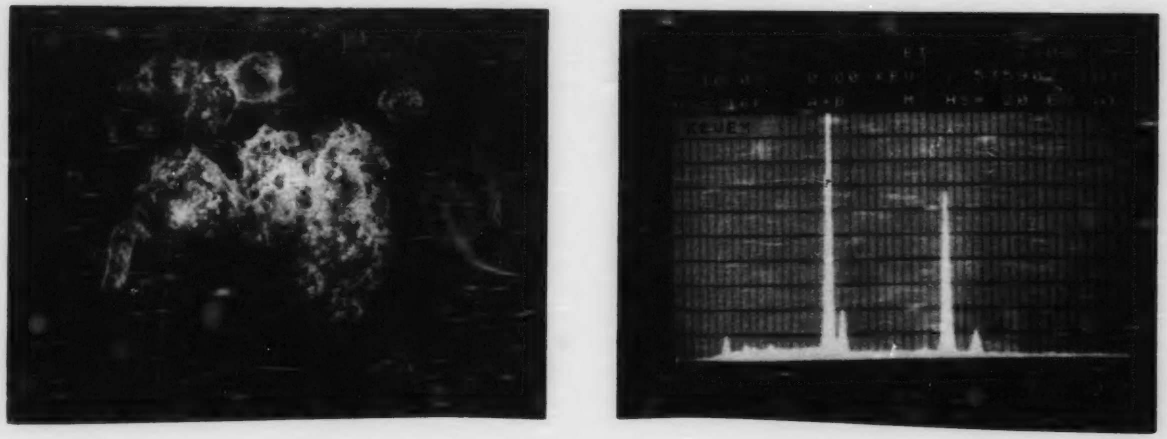
4.3.1.2.3 Basic Oxygen Furnace Samples -- The two basic oxygen furnace samples were similar. The No. 10 sample showed agglomerated masses and carbon flakes while the No. 11 sample showed large spherical particles and agglomerated masses. In the X-ray analysis, the No. 10 sample showed Si, Pb, Cl, and K in addition to S, Ca, Mn, Fe, and Zn. The No. 11 sample showed these latter elements and Mg and Ni. A summary of the particle characteristics is given in Table 7.

TABLE 7. MAJOR CHARACTERISTICS OF BASIC OXYGEN FURNACE SAMPLES

Characteristics	Sample No. 11	Sample No. 10
Consistency	Large spherical particles and agglomerated masses of smaller particles	Agglomerated masses and large irregular carbon flakes
X-ray Analysis	S, Ca, Mn, Fe, Ni (trace), and Zn (trace)	Si, S, Pb, Cl, K, Ca, Mn, Fe, Zn
Particle Size Range	Up to 35 μm	Carbon -- up to 740 μm Spherical Iron -- 0.02 - 0.24 μm

The No. 11 Sample -- Figure 16 shows the No. 11 BOF sample and the results of the X-ray analysis. The sample is characterized by large spherical and irregular-shaped particles and by agglomerated masses of smaller particles. The X-ray spectrum shows more calcium than iron with small amounts of S, Mn, Ni, and Zn.

The No. 10 Sample -- Examination of the No. 10 basic oxygen furnace sample revealed basically two types of particles--agglomerated, spherical iron and irregular, flaky carbon. Figure 17 shows photographs of the agglomerated masses at various magnifications from 460 to 23,000X and an X-ray spectrum of the sample. Examination of the agglomerated sample revealed mostly spherical iron particles of the size range of 0.02 to 0.24 μm (Figure 17c). X-ray analysis revealed very little calcium plus Si, S, Pb, Cl, K, Mn, Fe, and Zn.



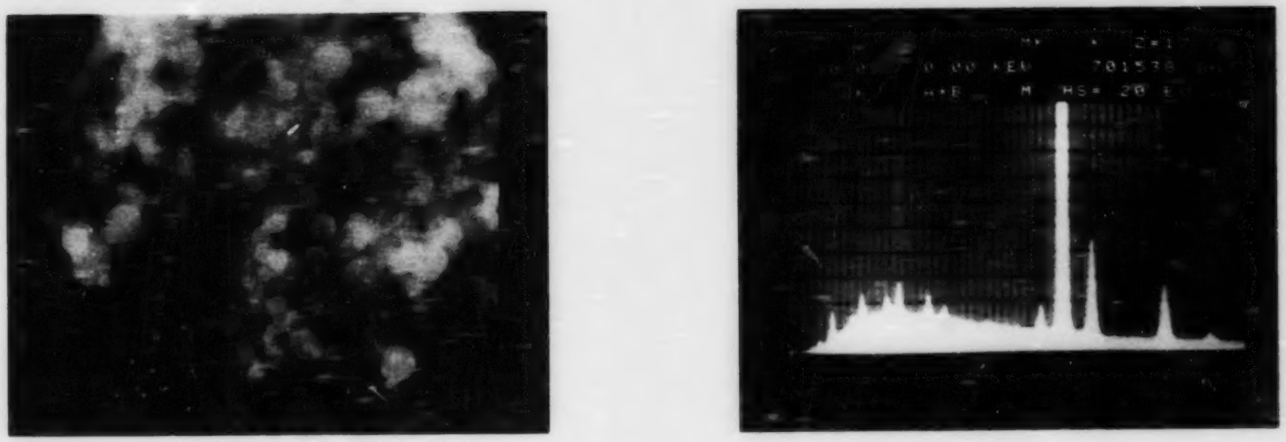
(a) Photo of sample at 576x.

(b) X-Ray of sample showing S, Ca, and Fe.

Figure 16. Electron microscopy examination of the No. 11 BOF sample.

(a) Photo of sample at 460x.

(b) Photo of sample at 4600x.



(c) Photo of sample at 23,000x. Shows distinct particles in the size range of 0.02 to 0.24 μ.

(d) X-Ray of sample showing Si, S, Pb, Cl, K, Ca, Mn, Fe, and Zn.

Figure 17. Examination of the No. 10 BOF sample.

Figure 18a shows a photograph of a carbon particle at 120X. An iron map (18b) confirms the composition of the agglomerates adhering to and lying around the carbon flake.

4.3.2 Specific Gravity

The specific gravity of the eighteen samples was determined and is presented in Table 8. These results represent a bulk specific gravity. The procedure employed is discussed in Appendix A.

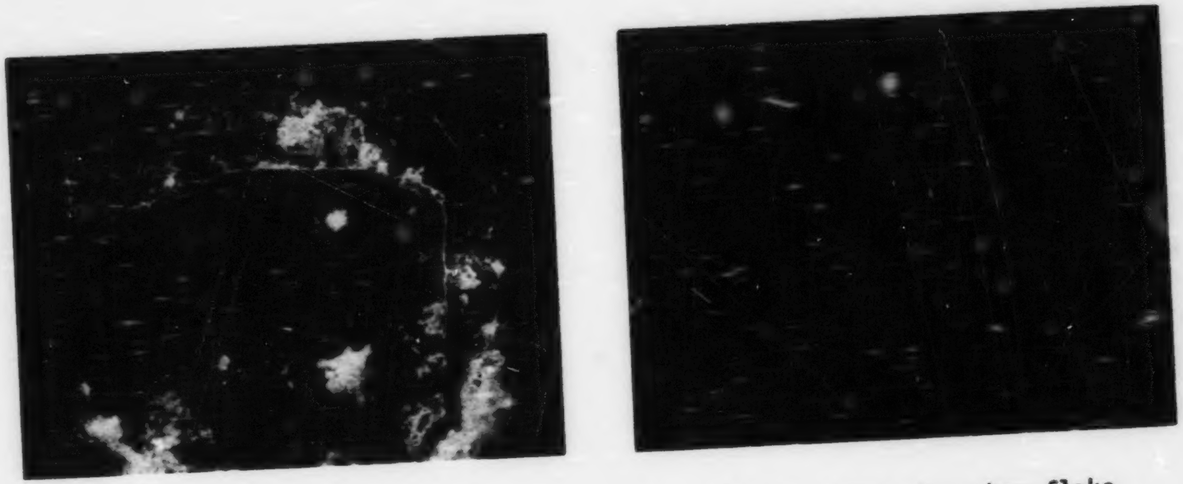
TABLE 8. SPECIFIC GRAVITY OF RESIDUE SAMPLES

Sample Number	Specific Gravity
1	4.07
2	3.59
3	5.20
4	3.86
5	4.40
6	4.06
7	4.22
8	3.90
9	4.06
10	4.29
11	4.75
12	4.12
13	4.57
14	3.99
15	4.24
16	3.77
17	4.12
18	4.26

4.3.3 Particle Size Analysis

Particle size analysis was attempted on each of the eighteen samples by a combination sieve/pipette technique. A description of the method employed and the raw data is given in Appendix B. After completing the size analysis of the first group of samples, electron microscopy results indicated that the pipette analysis was providing grain size values much coarser than those of the actual samples. Analysis was discontinued at this point.

Data bias such as exhibited by the pipette analysis usually can be traced to incomplete initial dispersion of the original sample and/or flocculation



(a) Photo of carbon flake at 120x.

(b) Iron map of carbon flake.

Figure 18. Photo and iron map of carbon flake and adhering iron agglomerates in the No. 10 BOF sample.

(or clumping) of the dispersed grains related to surface charges. Incomplete dispersion probably was not a major factor because of the method employed. Two identical samples were dispersed in 1000 ml cylinders. The first had been soaked overnight, then stirred gently with a glass rod before introduction into the cylinder. The second, after soaking overnight, was treated to 10 minutes in a laboratory blender before introduction into the cylinder. No visual difference could be detected in their rate of settling.

Clumping of individual particles to create larger grains while within the dispersed mixture appears to be the source of the apparent coarse bias of the pipette data. The cause of this flocculation of the sample material is not known, and could not be controlled by addition of standard peptizers to the mixture. In the initial pipette analysis, some sodium oxalate was added as a deflocculant agent. When it later became apparent that flocculation nonetheless had occurred, some brief comparative experiments were run using two different samples. Varying concentrations of hydrochloric acid, sodium oxilate, and Calgon had no visually detectable effect on rate of sedimentation vis-a-vis water alone. Addition of NH_4OH, however, caused almost instantaneous flocculation and settling. Non-water suspensions, including Varsol and grain alcohol, were no improvement and would not disperse.

The immediate flocculation in NH_4OH, but lack of response to other peptizers might suggest clumping is a result of processes other than true flocculation. The volume of material suspended was sufficiently small to minimize dragging of smaller grains in the wake of coarser grains. Therefore, the rate of clumping would seem to preclude aggregation by simple mutual mass attraction. The physical character of the settling clumps under low magnification suggests a loose chain-like or lattice-like arrangement of particles. Perhaps, with the high iron content of the grains, they may be acting as small natural magnets.

The results of the completed size analysis are shown in Table 9.

The grain size data based on wet sieving reflects true grain size percentages. Size data of the finer material, based on pipette, at best must be considered as a relative "effective sedimentation grain size" in water. Here, the flocculation characteristics of a sample seem to be consistent enough to indicate that the material will settle out in water as if it had the tabulated

TABLE 9. PARTICLE SIZE ANALYSES (PERCENT)

Sample Number	SIZES								Sample Weight (gm)
	<4*	4-5	5-6	6-7	7-8	8-9	9-10	10-11[1]	
	>62.5	62.5-31.2	31.2-15.6	15.6-7.8	7.8-3.9	3.9-1.95	1.95-.975	.975-.487[2]	
1	2.2	↔	↔						23.955
2	2.7	↔	↔						26.889
3	0.6	1.7	96.4	0.5	0.9	---	---	---	30.588
4	0.4	↔	↔	↔					25.250
5	93.8	3.4	1.0	1.3	0.2	0.3	---	---	95.065
6	1.5	↔	↔						25.867
7	2.1	4.9	88.0	4.8	0.2	---	---	---	19.925
8	2.1	↔	↔						29.190
9	24.8	↔	↔	↔					26.681
10	14.6	6.9	17.4	60.8	0.3	---	---	---	26.722
11	70.6	12.4	14.9	1.8	0.3	---	---	---	29.875
12	7.2	↔	↔	↔	↔				26.611
13	3.8	5.5	70.7	19.3	0.3	0.4	---	---	24.728
14	1.7	↔	↔	↔					25.353
15	4.9	7.8	12.4	42.1	31.2	1.6	---	---	17.923
16	24.1	↔	↔						32.183
17	4.2	↔	↔						26.810
18	1.0	0.9	11.3	86.1	0.5	0.1	---	---	26.313
Replicates									
7	2.1	4.9	88.0	4.8	0.2	---	---	---	19.925
7R	2.2	4.9	88.8	0.6	3.4	0.2	---	---	18.455

continued

TABLE 9 (Cont'd)

Sample Number	SIZES								Sample Weight (gm)
	<4*	4-5	5-6	6-7	7-8	8-9	9-10	10-11[1]	
	>62.5	62.5-31.2	31.2-15.6	15.6-7.8	7.8-3.9	3.9-1.95	1.95-.975	.975-.487[2]	
15	4.9	7.8	12.4	42.1	32.1	1.6	---	---	17.923
15R	4.6	3.7	0.7	50.0	39.7	0.8	0.5	---	19.667
2	2.7	←——	——→						26.889
2R	2.7	←——	——→						30.037

---

*by sieve; ←——→ no pipette analysis, arrow indicates approximate effective pipette size range.

[1] phi scale

[2] micrometer scale

grain size distribution. One caution in such a usage is that flocculation rate may be concentration sensitive. In the event it is not, the data show that if introduced into water systems, the residue will settle much faster than its grain size (true) would suggest.

The problems in obtaining particle size data led to an examination of the literature for supplementary information. Results of this examination follow.

OPEN HEARTH FURNACE DUST — **REFERENCE**

DATA

Size (µm)	Weight Percent	Reference
50 percent less than 5 micrometers		1
Size (µm)	Weight Percent	8
0-5	64.70	
5-10	6.79	
10-20	11.90	
20-44	8.96	
>44	7.65	
1-3	7.3	9
0.5-1	28.4	
0.15-0.5	49.5	
-0.15	14.8	
+5	6	9
1-5	34	
-1	60	

ELECTRIC FURNACE DUST

Size (µm)	Weight Percent*	Reference
93 percent less than 0.5 micrometers		1
Size (µm)	Weight Percent*	8
0-5	67.9-71.9	
5-10	6.8-8.3	
10-20	6.0-9.8	
20-44	7.5-9.0	
>44	6.3-6.5	

*Based on two furnaces

Size (µm)	Weight Percent*	Reference
0-5	43.3-72.0	8
5-10	10.5-37.8	
10-20	2.7-8.0	
20-40	1.6-14.6	
>40	0 -18.0	

*Based on five furnaces

		REFERENCE
90 to 95 percent less than 0.5 micrometer		10
90 percent less than 1.0 micrometer		10
100 percent less than 3.0 micrometer		10
70 to 71.9 percent less than 0.5 micrometer		10
BASIC OXYGEN FURNACE DUST		
85 percent less than 1.0 micrometer		1
Size (μm)	Weight Percent	10
<0.5	20	
0.5-1.0	65	
1.0-15.0	15	
<5	8.9	
5-10	9.1	
10-20	39.9	
20-30	28.8	
>30	13.3	

4.3.4 Chemical Analysis

Each of the 18 residue samples was subjected to elemental analysis by spark source mass spectrometry (SSMS). The results are shown in Table 10. The preparation and analysis procedures for the samples are described in Appendix C.

The determination of some elements is precluded or restricted by interferences or other factors. Those elements thus influenced are as follows:

Indium, Erbium, and Tantalum--used as source parts and internal standards

Fluorine ($^{19}F^+$)--overlap by $^{57}Fe^{+3}$

Sulfur--zinc and oxygen interferences

Aluminum--interference from $^{54}Fe^{+2}$; therefore, estimated by $^{27}Al^{+2}$ line. Estimates good to order of magnitude only.

Selenium--suffers interference from FeC_2^+ species and only estimated when Se 77, 78, and 80 isotope ratios are within experimental uncertainty.

TABLE 10. RESULTS OF SSMS ANALYSIS OF STEELMAKING RESIDUES (μg/g)

	OPEN HEARTH						ELECTRIC							BASIC OXYGEN				
Element	1	2	3	8	14	17	4	5	6	7	12	13	18	9	10	11	15	16
Aluminum	1,700	1,500	1,800	730	1,400	1,400	4,100	2,700	400	500	1,400	1,370	4,500	66	1,100	730	450	1,400
Antimony	44	106	40	--	89	54	109	--	78	185	140	260	74	--	20	--	21	--
Arsenic	210	550	78	37	210	75	.89	8.6	164	200	145	250	750	57	30	136	81	25
Barium	89	--	24	17	30	74	336	42	364	470	272	600	30	132	70	--	39	35
Bismuth	--	--	--	--	40	--	103	--	41	205	--	84	--	--	--	--	--	--
Cadmium	--	--	--	--	--	350	--	--	--	1,044	710	900	--	--	--	--	--	--
Calcium	12,300	7,700	7,330	3,390	18,600	23,700	103,000	39,000	192,000	92,800	89,400	68,200	11,000	61,500	35,000	71,000	35,900	91,600
Cerium	--	--	--	15	--	70	46.5	--	20	6.1	6	--	--	--	--	--	--	--
Cesium	2.4	--	--	--	--	1.3	4.4	--	2.8	--	3.6	4	--	3	--	--	--	--
Chlorine	750	--	530	540	1,000	3,500	2,130	274	15,300	--	7,630	16,000	750	984	1,700	400	1,500	430
Chromium	1,900	1,020	2,820	826	1,260	1,810	101,000	7,770	27,900	2,300	8,500	3,120	1,090	100	420	1,220	563	330
Cobalt	100	31	127	29	103	135	3,100	37	1,600	590	266	2,200	56	590	37	1,450	900	440
Copper	7,850	2,550	1,260	215	2,470	1,720	7,550	520	4,070	5,730	5,500	2,200	2,370	950	650	450	600	140
Gallium	155	121	61	71	240	55	250	17	93	47	76	130	134	50	24	700	760	75
Germanium	--	204	120	105	250	74	68	--	58	24	52	78	126	--	79	--	87	16
Iron	Major	Major	Major	Major	Major	445,000	392,700	Major	479,000	310,000	402,020	400,000	Major	Major	Major	Major	Major	Major
Lanthanum	--	--	--	--	--	--	8.9	--	--	--	--	--	--	--	--	--	--	--
Lead	1,540	7,150	4,120	104	10,300	17,600	4,825	513	17,200	108,600	25,700	39,570	6,700	105	4,700	2,100	6,100	790
Magnesium	8,300	3,600	4,660	3,050	17,000	38,900	32,000	4,520	66,700	11,000	44,000	20,100	9,700	2,420	8,000	33,700	8,530	17,700
Manganese	8,620	9,620	7,990	2,000	7,600	132,000	175,000	10,200	92,400	46,000	91,400	45,700	10,200	5,000	25,900	11,500	39,500	13,900
Molybdenum	71	112	133	74	200	54	6,050	108	8,500	76	446	100	550	--	54	--	64	68
Nickel	320	260	250	100	300	116	46,400	730	420	210	2,070	310	300	39	69	100	176	67
Niobium	--	--	--	--	--	--	160	21	--	13	36	29	--	--	--	--	--	--
Phosphorus	3,500	1,240	830	800	2,420	2,320	--	900	1,120	955	890	1,550	2,230	1,040	840	1,660	2,630	470
Potassium	11,500	13,300	4,070	3,920	1,450	14,700	54,000	232	17,900	9,350	25,600	13,000	14,800	4,270	5,270	380	1,620	4,900
Rubidium	--	32	15	16	7	41	90	--	78	62	74	52	45	24	72	--	6	13
Scandium	3.1	6.1	7.5	2.9	17	15	5	--	20	12	39	39	8	19	6.3	66	7.8	17
Selenium	--	--	--	--	--	--	2,040	--	156	360	--	630	--	--	--	--	--	--
Silicon	8,850	8,500	8,300	4,600	4,350	7,350	11,000	7,500	66,500	55,000	43,900	16,000	11,600	14,300	17,700	30,000	75,000	89,040
Silver	35	26	20	--	20	30	116	--	60	130	80	170	34	--	30	--	37	--
Sodium	5,520	3,550	8,000	2,990	7,340	14,000	31,000	320	16,300	8,950	26,400	12,200	10,900	4,740	5,190	800	690	1,630
Strontium	29	31	18	14	195	55	91	31	171	124	147	140	20	34	43	290	51	270
Tellurium	--	650	--	--	--	--	19	--	--	--	105	--	--	--	--	--	--	--
Tin	113	233	195	--	500	200	100	19	769	1,920	865	730	385	--	65	--	81	--
Titanium	296	238	290	104	300	320	290	250	700	680	1,100	866	765	367	450	1,420	800	840
Vanadium	410	172	104	44	175	170	550	195	112	100	103	89	70	100	154	290	576	113
Yttrium	--	--	--	--	--	-- --	40	--	18	8	7	11	--	--	--	--	--	--
Zinc	5,570	81,700	182,000	813	76,900	97,900	12,400	4,040	140,000	294,000	325,000	Major	62,900	1,700	99,000	4,200	54,900	3,900
Zirconium	--	--	--	88	--	-- --	67	21	--	90	100	130	--	--	--	--	--	--

Cadmium--uncertainty associated with results because of known volatility losses in sparking electrodes.

Sample No. 4--high Cr, Ni, Fe, and Mo precluded normal determination of Mg, Si, and Ti due to overlap of +2 masses, and results good only to an order of magnitude.

A search of available literature for comparative analysis was conducted. The results of this search are presented in Table 11.

TABLE 11. ELEMENTAL COMPOSITION OF STEELMAKING DUSTS BASED ON REPORTED VALUES[6,11,12,13,14]

	CONCENTRATION (μg/g)		
Element	Open Hearth	Electric	Basic Oxygen
Aluminum	400 - 6700	1500 - 42,000	trace - 36,000
Antimony	<100	<100	<100 - <200
Arsenic	<200 - <300	200	<200
Calcium	4800 - 26,000	600 - 302,000	3000 - 237,000
Carbon	2300 - [illegible],000	2800 - 74,000	trace - 6100
Chromium	----	1400 - 97,000	----
Copper	920 - 1000	1000 - 2700	80 - 500
Fluoride	15,200	7500 - 12,700	10,000 - 13,000
Iron	270,000 - 680,000	217,000 - 558,000	324,000 - 866,000
Lead	500 - 25,000	trace - 51,000	trace - 18,000
Magnesium	2000 - 186,000	4000 - 126,000	800 - 86,000
Manganese	200 - 4900	5000 - 64,000	800 - 20,000
Nickel	----	300 - 29,000	----
Phosphorous	820	740 - 2900	1000
Potassium	5200 - 25,000	1000 - 32,000	100 - 12,000
Selenium	<100	<100	<100
Silicon	2500 - 110,000	1000 - 46,000	1900 - 130,000
Sodium	1300 - 9000	500 - 41,000	<100 - 4700
Sulfur	1000 - 27,000	200 - 10,000	<100 - 20,000
Tin	<100	<100	trace - 4600
Zinc	300 - 151,000	trace - 248,000	trace - 151,000

4.3.5 Source of Dust Constituents

The substances that compose the dusts collected by air pollution control equipment can originate in the ore charged to the blast furnace, in the scrap charged to the steelmaking furnace, or in additives used to control the process or impart special properties to iron or steel. A listing of the probable sources of the various substances is given in Table 12. Source identification is described below.

TABLE 12. PROBABLE SOURCES OF SUBSTANCES COMPRISING STEELMAKING DUSTS

	SOURCE			
Substance	Ore	Scrap	Additive	Reference
Aluminum	x		x	15,16
Antimony	x			17
Arsenic	x			14,15, 17
Calcium	x		x*	15
Chromium	x	x	x	14,15,16
Cobalt	x		x	15,16
Columbium			x	16
Copper	x	x	x	14,15,16
Iron	x	x		14,15
Gold	x			16
Lead	x	x	x	14,15,16
Magnesium	x		x**	15,16
Manganese	x	x	x	14,15,16
Mercury		x		14
Molybdenum		x	x	16
Nickel	x		x	15,16
Phosphorous	x			14,15,16,17
Potassium	x			14
Selenium	x			14,17
Silica	x		x**	15,16
Silver	x			16
Sodium	x			14
Sulfur	x			14,15
Tin	x		x	15,16
Titanium	x		x	15,16
Tungsten			x	16
Vanadium	x		x	15,16.17
Zinc	x	x		14,15

*Flux **Additive and flux

4.3.5.1 Ores--

The iron ores used in steelmaking come from a variety of U.S. and foreign sources. In 1974, total consumption of iron ore was 131.1 x 10^9 kg (144.5 x 10^6 net tons), of which approximately 65 percent came from U.S. sources and 35 percent from foreign sources.[3] Approximately 85 percent of the U.S. production came from the Lake Superior District. Here banded, sedimentary ore deposits are predominately composed of iron and silica with small amounts of alumina, sodium, potassium, and minor elements.[18] The major ranges in this district are the Mesabi, Cuyuna, Gogebic, Marquette, and Menominee.

Both the occurrence and the quantities of the various metals vary from one iron deposit to another. Factors involved in these variations include type of deposit, parent material of the deposit, and post depositional geological influences on the deposit, including metamorphism. These variations also occur within a single deposit. Examples of these quantity variations include:[15]

iron	32-55.5 %
silica	3-45 %
aluminum	0.8-2.6 %
calcium	0.02-2.3 %
magnesium	0.02-3.0 %
phosphorous	0.04-0.54 %
manganese	0.17-4.5 %

4.3.5.2 Scrap--

Steep scrap can originate from a variety of sources, although two grades of scrap exist. Number one scrap is considered essentially "pure", while number two scrap is considered "contaminated" and may contain copper wire, rubber, wood, etc. Table 13 shows the 1974 consumption of scrap and pig iron by type of furnace.[3]

Depending on the type of scrap used, it is possible for most elements to originate from the scrap. For example, lead and zinc probably originate from galvanized scrap, while copper probably comes from the copper wiring in auto scrap.

TABLE 13. 1974 CONSUMPTION OF SCRAP AND PIG IRON BY IRON AND STEEL FURNACES[3]

Furnace Type	CONSUMPTION (10^9 Kg) Scrap	Pig Iron	Total
Open Hearth	17.1	21.2	38.4
Basic Oxygen	24.0	59.3	83.4
Electric	26.2	1.0	27.2
Blast	4.0	---	4.0
Subtotal	71.3	81.5	153.0
Industry Total*	72.7	83.9	156.7

*Includes consumption by cupolas, direct casting, and by other furnaces. Totals may not equal due to rounding off.

4.3.5.3 Additives --

Certain substances are added to the furnaces to control the process, to impart special properties to the iron or steel, and to control iron or steel properties. Table 14 lists these additives and their uses.

TABLE 14. ADDITIVES AND THEIR USES[16]

Substance	Use
Aluminum	Control grain size and remove impurities and gases
Calcium	Basic flux in form of limestone (calcium carbonate) and neutral flux in form of fluorspar (calcium fluoride)
Chromium	Resist corrosion, harden, and increase high-temperature strength
Cobalt	Increase high-temperature strength and make permanent magnet steels
Columbium	Resist heat,strength, and improve mechanical properties

continued

TABLE 14 (Cont'd).

Substance	Use
Copper	Improve machinability of iron and resist atmospheric corrosion of steel
Lead	Improve machinability
Magnesium	Basic flux in form of dolomite (magnesiun carbonate) and improve strength and ductibility of cast iron
Manganese	Remove gases from steel (small amounts), increase strength and toughness (1-2 percent Mn), and greatly increase toughness and abrasion resistance (12 percent Mn)
Molybdenum	Decrease temper brittleness and increase strength, ductibility, and shock resistance
Nickel	Increase toughness without brittleness
Silica	Acid flux, deoxidizer, and increases resistance to corrosion, heat, and wear
Tin	Resist wear in iron
Titanium	Control grain size and remove gases and impurities
Tungsten	Increase high temperature strength
Vanadium	Increase strength, ductibility, and resiliency

Table 15 shows the 1974 consumption of fluxes by the steel industry.[3] Consumption information for the other additives could not be located.

TABLE 15. 1974 CONSUMPTION OF FLUXES[3]

	CONSUMPTION (10^6 Kg)				
Furnace Type	Fluospar	Limestone	Lime	Other	Total
Blast	---	13,316.8	---	---	13,316.8
Open Hearth	88.0	1,469.7	456.3	216.8	2,230.8
Basic Oxygen	412.8	594.2	5,963.0	706.7	7,685.8
Electric	83.4	244.9	796.5	73.5	1,198.4
TOTAL	584.2	15,625.6	7,215.8	997.0	24,431.8

SECTION 5

SOLUBILIZATION TESTS

A major portion of this study was devoted to an examination of the possibility for water extraction of certain metals and organic compounds from the steelmaking furnace residues, since these residues are exposed to water at their disposal sites.

5.1 PROCEDURES AND RESULTS

Each of the 18 samples was subjected to 10 successive water washings by the procedures outlined in Appendix D. After each washing, a portion of the solute was removed and analyzed by atomic absorption for antimony, arsenic, cadmium, chromium, cobalt, lead, manganese, mercury (both total and inorganic), nickel, selenium, vanadium, and zinc. Cumulative solubilization data for these metals are presented in Tables 16 through 27. Arsenic was not detected in any of the samples. The pH values for each sample and solubilization run are presented in Table 28. The initial pH of the deionized water was 6.7.

A new one-wash solubilization test was performed on each of the 18 samples for detection of organics in the solutes. To analyze for the presence of organic compounds, a carbon analysis was performed. This was followed by a gas chromatography-mass spectrometry analysis of selected samples. Additional parameters such as conductivity and acidity/basicity were also determined. The results of these analyses are presented in Table 29 and are followed by a discussion of specific organic compounds identified by gc-ms in each sample.

TABLE 16. SOLUBILIZATION DATA FOR ANTIMONY

Furnace Type	Sample Number	CUMULATIVE CONCENTRATION (µg)										Total Concentration (µg metal/g residue)
		Run Number										
		1	2	3	4	5	6	7	8	9	10	
Open Hearth	1	4,914.0	4,914.0	5,803.0	6,476.2	7,483.5	8,184.6	8,601.5	9,819.8	9,819.8	10,693.4	85.55
	2	5,310.0	6,087.0	6,748.5	7,681.5	8,522.3	8,734.8	8,734.8	9,638.9	9,638.9	9,638.9	77.11
	3	4,100.0	4,100.0	4,500.4	4,727.2	5,213.2	5,505.3	5,505.3	5,988.9	5,988.9	6,841.5	57.73
	8	2,363,4	2,673.9	2,673.9	2,673.9	3,142.0	3,208.0	3,851.5	3,851.5	3,851.5	3,851.5	30.81
	14	966.0	966.0	1,896.0	1,896.0	1,937.4	2,508.9	2,556.6	2,556.6	4,806.2	4,806.2	38.45
	17	4,367.6	4,367.6	5,544.6	5,694.8	5,761.2	6,527.9	7,461.6	7,461.6	7,782.5	7,782.5	62.26
Electric	4	5,338.0	5,338.0	5,395.4	5,395.4	5,612.4	5,836.4	5,836.4	6,599.6	6,599.6	7,625.4	61.00
	5	1,529.5	1,529.5	2,833.0	3,366.0	4,035.9	4,166.8	4,934.4	5,444.0	5,759.8	5,759.8	46.08
	6	6,842.5	6,842.5	10,044.1	10,120.3	10,120.3	10,377.7	11,190.2	11,582.2	11,740.6	11,939.1	95.51
	7	6,670.0	6,670.0	8,779.7	8,813.2	9,289.0	9,663.4	10,457.5	11,776.7	11,776.7	13,448.3	107.59
	12	7,840.0	8,248.0	8,378.8	8,378.8	9,098.8	9,438.8	10,182.8	10,182.8	11,153.0	11,675.1	93.40
	13	2,352.0	2,352.0	4,586.0	5,087.4	5,600.1	6,240.6	7,998.0	8,282.2	9,585.3	9,665.1	77.32
	18	2,387.0	2,387.0	2,387.0	2,407.2	2,407.2	2,554.8	2,668.4	3,193.8	3,206.5	3,490.7	27.93
Basic Oxygen	9	1,577.6	2,729.6	2,837.5	2,837.5	3,611.0	4,213.0	5,413.6	5,413.6	6,326.2	6,742.2	53.94
	10	3,900.4	3,900.4	6,146.8	6,195.8	6,238.5	6,689.7	8,087.1	8,087.1	8,688.8	8,688.8	69.51
	11	3,900.0	3,900.0	6,555.0	12,203.4	12,203.4	12,487.1	14,035.9	14,035.9	14,290.9	14,290.9	114.33
	15	633.6	633.6	1,004.4	1,004.4	1,395.0	1,395.0	1,632.6	1,639.4	1,909.7	1,909.7	15.28
	16	1,626.0	1,857.0	1,861.7	1,861.7	1,873.7	2,148.1	2,361.1	2,626.3	2,914.5	3,862.5	30.90

TABLE 17. SOLUBILIZATION DATA FOR CADMIUM

Furnace Type	Sample Number	CUMULATIVE CONCENTRATION (µg)										Total Concentration (µg metal/g residue)
		Run Number										
		1	2	3	4	5	6	7	8	9	10	
Open Hearth	1	1,207.5	1,207.5	1,264.7	1,324.1	1,387.8	1,425.9	1,447.5	1,480.2	1,488.0	1,488.0	11.90
	2											
	3											
	8											
	14	89.3	89.3	97.0	115.8	126.9	133.2	144.4	150.6	150.6	150.6	1.20
	17	1,220.0	1,220.0	1,244.6	1,244.6	1,244.6	1,252.1	1,252.1	1,252.1	1,252.1	1,252.1	10.02
Electric	4											
	5											
	6	15.3	15.3	15.3	15.3	15.3	15.3	15.3	15.3	15.3	15.3	0.12
	7											
	12											
	13	246.0	246.0	246.0	246.0	246.0	246.0	246.0	246.0	246.0	246.0	1.97
	18	514.6	514.6	514.6	514.6	514.6	514.6	514.6	514.6	514.6	514.6	4.12
Basic Oxygen	9											
	10											
	11	0.0	0.0	0.0	15.7	15.7	15.7	15.7	15.7	15.7	15.7	0.13
	15											
	16											

TABLE 18. SOLUBILIZATION DATA FOR CHROMIUM

Furnace Type	Sample Number	CUMULATIVE CONCENTRATION (μg)										Total Concentration (μg metal/g residue)
		Run Number										
		1	2	3	4	5	6	7	8	9	10	
Open Hearth	1	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5	0.08
	2	22.5	42.5	42.5	42.5	42.5	57.2	71.7	71.7	71.7	71.7	0.57
	3	18.0	18.0	29.9	29.9	35.3	37.0	40.6	40.6	40.6	40.6	0.32
	8											
	14											
	17											
Electric	4	13,600.0	16,507.0	16,507.0	17,553.4	17,553.4	17,553.4	17,553.4	17,553.4	17,903.2	18,081.6	144.65
	5	0.0	0.0	55.3	145.5	285.6	440.8	606.4	779.3	945.6	1,060.8	8.49
	6	1,147.5	1,169.3	1,613.5	1,695.4	1,695.4	1,732.1	1,788.3	1,835.9	1,922.3	2,093.0	16.74
	7	12.8	12.8	12.8	18.8	25.3	25.3	29.3	29.3	29.3	53.2	0.43
	12	5,985.0	5,985.0	5,985.0	6,231.0	6,231.0	6,231.0	6,318.6	6,396.2	6,445.5	7,201.4	57.61
	13	8.4	25.5	64.8	99.7	107.0	127.2	137.3	159.6	159.6	188.9	1.51
	18	0.0	46.7	46.7	46.7	46.7	46.7	46.7	46.7	46.7	46.7	0.37
Basic Oxygen	9											
	10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	29.7	0.24
	11											
	15											
	16	109.2	109.2	109.2	109.2	109.2	112.0	112.0	113.6	121.5	125.1	1.00

TABLE 19. SOLUBILIZATION DATA FOR COBALT

Furnace Type	Sample Number	CUMULATIVE CONCENTRATION (μg) Run Number 1	2	3	4	5	6	7	8	9	10	Total Concentration (μg metal/g residue)
Open Hearth	1	525.0	693.0	1,124.8	1,124.8	1,379.8	1,552.0	1,632.7	1,973.3	1,973.3	2,376.5	19.01
	2	1,020.0	1,251.0	1,251.0	1,359.9	1,787.6	1,787.6	1,787.6	1,787.6	1,787.6	1,787.6	14.30
	3	557.6	557.6	803.3	851.9	851.9	851.9	1,170.5	1,170.5	1,170.5	1,170.5	9.36
	8	397.8	397.8	397.8	397.8	397.8	397.8	397.8	397.8	593.6	641.0	5.13
	14	0.0	230.4	230.4	230.4	230.4	230.4	230.4	448.8	600.8	600.8	4.81
	17	805.2	1,179.3	1,414.7	1,414.7	1,423.0	1,525.9	1,525.9	1,782.1	1,864.9	1,864.9	14.92
Electric	4	958.8	958.8	958.8	1,007.9	1,035.9	1,035.9	1,369.4	1,433.0	1,433.0	1,433.0	11.46
	5	226.1	226.1	226.1	226.1	226.1	226.1	226.1	499.1	604.4	922.9	7.38
	6	969.0	1,125.6	1,125.6	1,125.6	1,346.7	1,346.7	1,346.7	1,640.7	1,640.7	1,839.2	14.71
	7	527.8	806.8	306.8	820.2	1,296.0	1,296.0	1,356.3	1,463.0	1,601.6	1,800.6	14.40
	12	1,288.0	1,288.0	1,309.8	1,657.8	1,657.8	1,657.8	1,657.8	1,823.4	1,854.2	1,854.2	14.83
	13	180.0	453.6	650.3	683.0	683.0	683.0	683.0	683.0	683.0	683.0	5.46
	18	465.0	465.0	465.0	510.5	510.5	510.5	510.5	794.5	845.3	845.3	6.76
Basic Oxygen	9	232.0	443.2	443.2	443.2	740.7	894.7	894.7	1,155.1	1,265.0	1,348.2	10.79
	10	656.6	656.6	1,031.0	1,129.0	1,129.0	1,241.8	1,282.6	1,302.4	1,340.6	1,419.8	11.36
	11	555.0	555.0	1,074.2	1,900.4	1,900.4	2,101.7	2,172.1	2,183.9	2,281.7	2,281.7	18.25
	15	88.0	181.0	304.6	304.6	304.6	304.6	304.6	461.0	461.0	742.6	5.94
	16	138.0	138.0	302.5	302.5	394.5	394.5	643.0	650.8	673.4	709.4	5.68

TABLE 20. SOLUBILIZATION DATA FOR LEAD

Furnace Type	Sample Number	CUMULATIVE CONCENTRATION (µg)										Total Concentration (µg metal/g residue)
		Run Number										
		1	2	3	4	5	6	7	8	9	10	
Open Hearth	1	210.0	476.0	780.8	1,071.2	1,275.2	1,422.8	1,611.1	1,611.1	1,727.7	1,772.5	14.18
	2	150.0	150.0	150.0	150.0	150.0	150.0	150.0	150.0	150.0	150.0	1.20
	3	82.0	114.1	186.9	186.9	186.9	186.9	186.9	186.9	186.9	186.9	1.50
	8											
	14	514.5	672.9	1,029.4	1,437.6	1,796.4	2,139.3	2,505.0	3,269.4	3,862.2	4,473.2	35.79
	17	305.0	395.3	727.0	727.0	727.0	801.8	801.8	904.3	904.3	904.3	7.23
Electric	4	68.0	68.0	92.6	92.6	92.6	92.6	92.6	92.6	92.6	92.6	0.74
	5	598.5	598.5	776.3	919.8	1,610.0	1,610.0	1,610.0	1,610.0	1,610.0	1,610.0	12.88
	6	195.5	195.5	207.1	207.1	207.1	207.1	207.1	207.1	207.1	207.1	1.66
	7	25,350.0	25,350.0	59,056.3	94,879.6	96,928.9	128,344.9	128,344.9	160,934.7	160,934.7	183,449.7	1467.60
	12	0.0	284.0	536.6	680.6	776.6	776.6	2,396.6	2,614.0	2,614.0	3,363.1	26.90
	13	144.0	144.0	1,324.2	1,324.2	1,544.0	1,781.9	1,781.9	2,066.1	2,619.4	3,710.0	29.68
	18	241.8	241.8	241.8	241.8	282.1	282.1	367.3	367.3	367.3	753.0	6.02
Basic Oxygen	9	0.0	0.0	282.2	282.2	282.2	317.2	317.2	317.2	317.2	317.2	2.54
	10	5,880.0	6,480.0	7,809.6	7,809.6	8,596.6	9,207.5	9,207.5	10,019.3	10,019.3	10,019.3	80.15
	11	4,380.0	6,823.6	7,449.0	7,449.0	8,687.4	9,062.6	9,837.0	10,031.7	10,078.4	10,078.4	80.63
	15	0.0	0.0	0.0	62.0	62.0	62.0	62.0	62.0	62.0	182.60	1.46
	16	0.0	270.6	270.6	270.6	270.6	270.6	270.6	333.0	333.0	333.0	2.66

TABLE 21. SOLUBILIZATION DATA FOR MANGANESE

Furnace Type	Sample Number	CUMULATIVE CONCENTRATION (μg)										Total Concentration (μg metal/g residue)
		Run Number										
		1	2	3	4	5	6	7	8	9	10	
Open Hearth	1	23,730.0	23,730.0	23,730.0	23,978.2	23,978.2	23,978.2	23,978.2	23,984.7	23,984.7	24,031.8	192.25
	2	4,875.0	4,875.0	4,875.0	4,948.1	4,948.1	4,974.2	5,006.5	5,020.9	5,020.9	5,038.3	40.31
	3	0.0	0.0	13.7	13.7	13.7	13.7	13.7	13.7	13.7	34.0	0.27
	8	0.0	3.5	8.7	8.7	8.7	8.7	8.7	8.7	8.7	32.4	0.26
	14	813.8	813.8	815.3	878.1	894.7	915.0	946.8	967.1	992.9	1,030.5	8.24
	17	24,400.0	24,400.0	25,069.8	25,069.8	25,069.8	25,069.8	25,069.8	25,080.1	25,080.1	25.080.1	200.64
Electric	4	74.1	74.1	81.5	81.5	84.3	89.1	107.5	107.5	110.7	159.7	1.28
	5	0.0	0.0	0.0	106.6	135.0	176.2	176.2	203.5	203.5	419.1	3.35
	6	399.5	399.5	399.5	399.5	399.5	399.5	399.5	428.9	428.9	273.9	2.19
	7	0.0	0.0	6.6	13.9	121.6	121.6	151.7	151.7	151.7	251.2	2.01
	12	15.4	15.4	92.8	92.8	97.6	97.6	220.0	495.3	495.3	617.9	4.94
	13	312.0	312.0	733.5	733.5	767.2	897.1	897.1	897.1	920.3	1,298.1	10.38
	18	979.6	979.6	979.6	979.6	988.2	995.6	1,052.4	1,063.8	1,099.3	1,275.9	10.21
Basic Oxygen	9	0.0	21.1	21.1	21.1	21.1	21.1	21.1	21.1	21.1	100.2	0.80
	10	0.0	0.0	8.6	14.2	14.2	14.2	14.2	41.0	41.0	41.0	0.33
	11	21.0	74.6	88.8	126.6	126.6	126.6	152.1	152.1	245.6	245.6	1.96
	15	113.5	113.5	113.5	251.2	327.4	327.4	327.4	343.1	413.8	834.9	6.68
	16	0.0	38.3	38.3	38.3	38.3	38.3	38.3	38.3	47.9	51.5	0.41

TABLE 22. SOLUBILIZATION DATA FOR INORGANIC MERCURY

Furnace Type	Sample Number	CUMULATIVE CONCENTRATION (μg)										Total Concentration (μg metal/g residue)
		Run Number										
		1	2	3	4	5	6	7	8	9	10	
Open Hearth	1											
	2											
	3											
	8											
	14											
	17											
Electric	4											
	5											
	6											
	7	290.0	290.0	290.0	290.0	290.0	290.0	290.0	290.0	290.0	290.0	2.32
	12	840.0	7,560.0	7,560.0	8,484.0	9,300.0	9,300.0	9,300.0	9,300.0	9,300.0	9,300.0	74.40
	13											
	18	744.0	744.0	992.4	1,694.4	1,993.4	2,108.2	2,108.2	2,108.2	2,108.2	2,108.2	16.87
Basic Oxygen	9											
	10											
	11											
	15											
	16											

TABLE 23. SOLUBILIZATION DATA FOR TOTAL MERCURY

Furnace Type	Sample Number	CUMULATIVE CONCENTRATION (μg)										Total Concentration (μg metal/g residue)
		Run Number										
		1	2	3	4	5	6	7	8	9	10	
Open Hearth	1											
	2											
	3											
	8											
	14											
	17											
Electric	4											
	5											
	6											
	7	1,508.0	1,508.0	1,909.5	1,969.8	2,188.4	2,581.8	2,581.8	3,590.6	3,590.6	3,590.6	28.72
	12	6,440.0	10,724.0	10,724.0	11,528.0	12,776	13,755.2	15,075.2	15,779	15,856	18,534.6	148.28
	13	420	636.6	917.6	917.6	917.6	917.6	917.6	917.6	917.6	917.6	7.34
	18	1,364	1,684	1,684	1,987	2,849.5	2,849.5	3,701.5	3,701.5	3,701.5	3,701.5	29.61
Basic Oxygen	9											
	10											
	11											
	15											
	16											

TABLE 24. SOLUBILIZATION DATA FOR NICKEL

Furnace Type	Sample Number	CUMULATIVE CONCENTRATION (µg)										Total Concentration (µg metal/g residue)
		Run Number										
		1	2	3	4	5	6	7	8	9	10	
Open Hearth	1	73.5	73.5	73.5	73.5	73.5	73.5	73.5	73.5	73.5	73.5	0.59
	2	285.0	285.0	285.0	285.0	285.0	285.0	285.0	285.0	285.0	285.0	2.28
	3											
	8											
	14	63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	0.50
	17	97.6	97.6	97.6	97.6	97.6	97.6	97.6	97.6	97.6	97.6	0.78
Electric	4	47.6	47.6	47.6	47.6	47.6	47.6	47.6	47.6	47.6	47.6	0.38
	5											
	6											
	7	40.6	40.6	40.6	40.6	40.6	40.6	40.6	40.6	40.6	40.6	0.32
	12											
	13	0.0	0.0	0.0	54.5	54.5	54.5	54.5	54.5	54.5	54.5	0.44
	18	31.0	31.0	31.0	31.0	31.0	31.0	31.0	31.0	31.0	31.0	0.25
Basic Oxygen	9											
	10											
	11	0.0	0.0	0.0	54.0	54.0	54.0	54.0	54.0	54.0	54.0	0.43
	15											
	16											

TABLE 25. SOLUBILIZATION DATA FOR SELENIUM

Furnace Type	Sample Number	CUMULATIVE CONCENTRATION (μg)										Total Concentration (μg metal/g residue)
		Run Number										
		1	2	3	4	5	6	7	8	9	10	
Open Hearth	1	420.0	420.0	534.3	573.9	637.7	637.7	637.7	637.7	637.7	637.7	5.10
	2	150.0	286.5	286.5	550.9	550.9	550.9	550.9	550.9	550.9	550.9	5.40
	3	82.0	210.4	210.4	364.3	364.3	364.3	417.4	417.4	417.4	417.4	3.34
	8	93.6	93.6	250.8	276.6	327.2	380.0	380.0	380.0	380.0	380.0	3.04
	14	997.5	997.5	997.5	997.5	1,121.7	1,121.7	1,121.7	1,121.7	1,121.7	1,121.7	8.97
	17	122.0	122.0	196.9	218.4	218.4	274.5	274.5	397.5	397.5	397.5	3.18
Electric	4	10,676.0	11,493.0	11,493.0	11,825.5	11,825.5	11,825.5	11,837.0	11,837.0	12,038.4	12,038.4	96.31
	5	133.0	226.0	364.3	364.3	547.0	696.6	696.6	696.6	696.6	696.6	5.57
	6	170.0	257.0	291.8	291.8	298.5	298.5	373.5	373.5	373.5	373.5	2.99
	7	203.0	203.0	363.6	363.6	363.6	609.6	609.6	609.6	609.6	609.6	4.88
	12	980.0	980.0	980.0	1,040.0	1,064.0	1,064.0	1,064.0	1,064.0	1,064.0	1,064.0	8.51
	13	162.0	162.0	162.0	314.6	446.5	446.5	446.5	446.5	446.5	446.5	3.57
	18	142.5	174.6	174.6	210.0	210.0	218.2	218.2	218.2	218.2	218.2	1.75
Basic Oxygen	9	58.0	67.6	92.5	150.6	150.6	150.6	150.6	150.6	150.6	150.6	1.20
	10	98.0	98.0	242.0	368.0	368.0	368.0	368.0	368.0	368.0	368.0	2.94
	11	300.0	300.0	300.0	440.4	440.4	440.4	440.4	440.4	440.4	440.4	3.52
	15	0.0	55.8	55.8	93.0	93.0	93.0	93.0	93.0	93.0	93.0	0.74
	16	0.0	59.4	59.4	59.4	59.4	59.4	59.4	59.4	59.4	59.4	0.48

TABLE 26. SOLUBILIZATION DATA FOR VANADIUM

Furnace Type	Sample Number	CUMULATIVE CONCENTRATION (μg)										Total Concentration (μg metal/g residue)
		Run Number										
		1	2	3	4	5	6	7	8	9	10	
Open Hearth	1											
	2											
	3											
	8											
	14											
	17											
Electric	4	428.4	428.4	428.4	428.4	428.4	428.4	451.4	451.4	451.4	451.4	3.61
	5											
	6											
	7	0.0	0.0	0.0	0.0	0.0	0.0	100.5	100.5	100.5	100.5	0.80
	12	182.0	182.0	182.0	182.0	182.0	182.0	182.0	182.0	182.0	182.0	1.46
	13											
	18	74.4	80.8	80.8	80.8	80.8	80.8	80.8	80.8	80.8	80.8	0.65
Basic Oxygen	9											
	10	107.8	107.8	107.8	107.8	107.8	107.8	107.8	107.8	107.8	107.8	0.86
	11	0.0	0.0	0.0	91.8	91.8	91.8	91.8	91.8	91.8	91.8	0.73
	15											
	16											

TABLE 27. SOLUBILIZATION DATA FOR ZINC

Furnace Type	Sample Number	CUMULATIVE CONCENTRATION (μg)										Total Concentration (μg metal/g residue)
		Run Number										
		1	2	3	4	5	6	7	8	9	10	
Open Hearth	1	96,600	96,600	102,924.6	102,924.6	110,549.1	111,557.7	123,904.8	123,904.8	124,601.4	127,132.6	1,017.06
	2	114.0	114.0	114.0	114.0	114.0	141.8	141.8	141.8	141.8	141.8	1.13
	3	41.0	630.6	714.3	964.6	964.6	1,713.3	1,730.1	1,730.1	1,730.1	2,211.2	17.69
	8	7.8	10.1	44.2	44.2	44.2	44.2	44.2	44.2	44.2	101.0	0.81
	14	65,625.0	65,625.0	65,625.0	80,084.7	83,134.5	85,166.5	87,344.8	89,435.2	91,198.4	92,722.9	742.18
	17	54,168.0	54,168.0	57,752.5	57,752.5	57,752.5	57,752.5	57,752.5	57,752.5	57,752.5	57,785.3	462.28
Electric	4	61.2	61.2	94.8	94.8	94.8	101.2	108.1	120.8	125.1	131.8	1.05
	5	266.0	266.0	390.4	960.3	1,199.9	1,285.9	1,346.5	1,402.9	1,457.6	1,844.7	14.76
	6	1,411.0	1,411.0	1,411.0	1,413.5	1,422.3	1,443.0	1,458.0	1,529.4	1,555.4	2,266.0	18.13
	7	783.0	783.0	1,164.1	1,237.1	1,856.4	1,856.4	2,099.6	2,099.6	2,099.6	2,656.8	21.25
	12	882.0	967.2	2,048.5	2,048.5	2,251.3	2,251.3	4,622.5	7,198.6	7,198.6	8,099.8	64.80
	13	936.0	936.0	8,531.4	8,531.4	10,542.9	12,861.5	12,861.5	13,728.3	14,099.6	19,940.9	159.53
	18	1,736.0	1,736.0	1,737.4	1,737.4	1,737.4	1,737.4	2,102.3	2,214.5	2,311.0	2,816.5	22.53
Basic Oxygen	9	7.5	23.9	44.6	58.6	62.9	62.9	76.8	76.8	99.6	126.7	1.01
	10	254.8	420.4	544.2	637.3	637.3	637.3	725.1	851.8	1,092.4	1,092.4	8.74
	11	133.5	281.0	364.8	1,157.0	1,157.0	1,255.8	1,320.9	1,368.7	1,424.0	1,424.0	11.39
	15	334.4	471.1	471.1	722.2	862.6	862.6	862.6	903.4	1,052.4	1,138.1	9.11
	16	0.0	291.1	291.1	291.1	297.5	300.8	300.8	303.9	303.9	369.9	2.96

TABLE 28. EFFECTS ON pH OF LEACHING TESTS

		pH OF SAMPLES BY LEACHING RUNS*									
Furnace Type	Sample Number	1	2	3	4	5	6	7	8	9	10
Open Hearth	1	7.2	7.2	7.3	7.4	7.6	7.1	7.4	6.0	6.4	6.4
	2	8.6	8.0	8.4	8.5	8.9	9.9	9.3	8.2	7.7	7.9
	3	9.5	7.4	8.7	9.5	9.1	9.3	9.0	9.2	7.9	8.2
	8	10.0	8.3	8.5	10.0	9.5	9.2	9.5	9.5	10.2	9.9
	14	5.7	7.1	7.0	7.2	7.2	6.8	6.8	6.8	7.3	6.2
	17	7.6	7.3	8.0	7.9	8.0	7.9	7.6	8.8	9.1	9.8
Electric	4	12.0	11.2	11.3	12.1	12.1	12.1	11.9	11.8	11.9	11.9
	5	12.4	11.7	11.6	11.9	11.8	11.1	10.7	10.9	11.4	11.4
	6	10.6	8.0	10.0	10.2	10.2	9.9	10.5	10.3	10.8	10.9
	7	12.8	12.5	1.21	12.6	1.25	11.8	11.9	11.8	12.2	12.1
	12	12.7	11.9	11.8	12.1	11.9	11.4	11.0	11.4	11.9	11.8
	13	8.9	8.4	9.3	10.8	10.8	10.5	10.5	10.4	11.0	11.0
	18	7.9	8.1	9.2	7.1	8.6	8.4	8.5	7.5	8.6	8.9
Basic Oxygen	9	12.7	12.3	12.3	12.4	12.5	11.5	11.9	11.6	12.4	12.3
	10	12.5	11.9	11.6	12.4	11.8	11.8	11.5	11.5	12.2	12.0
	11	12.6	12.1	11.6	12.4	12.4	11.5	11.6	11.6	12.4	12.2
	15	10.5	8.2	9.6	9.7	9.1	9.0	9.0	8.2	9.0	8.7
	16	12.7	12.2	11.6	12.3	12.3	11.3	11.9	11.4	12.3	12.4

*Initial pH of deionized water was 6.7.

TABLE 29. RESULTS OF ANALYSES PERFORMED ON SECOND SET OF LEACHATES

Furnace Type	Sample Number	Carbon Analysis (mg/ℓ)		pH	Acidity/Basicity (equivalents KOH/ℓ)	Conductivity (m mhos/cm)
		Inorganic	Organic			
Open Hearth	1	3	19	7.0	0.00	11.5
	2	9	18	7.2	0.64	8.6
	3	7	21	8.6	0.64	10.8
	8	5	27	9.2	0.03	5.7
	14	0	16	6.0	0.00	2.3
	17	0	11	6.5	0.00	11.1
Electric	4	26	310	11.9	1.71	24.5
	5	2	23	12.4	1.69	5.1
	6	10	166	9.2	0.06	20.5
	7	14	41	12.8	7.01	44.3
	12	21	279	12.6	3.10	29.8
	13	0	59	7.3	0.01	20.5
	18	0	181	6.5	0.00	17.0
Basic Oxygen	9	4	58	12.6	2.74	13.8
	10	2	21	12.5	2.58	14.6
	11	0	35	12.5	2.47	7.2
	15	4	13	8.1	0.01	0.8
	16	2	12	12.5	3.36	13.1
	Blank	0	4	6.5	--	3.0*

*Expressed as μ mhos.

The samples showing the highest TOC (numbers 4, 6, 12, and 18) were analyzed by gc-ms. The results showed the types of products that would be expected from the distillation of mineral-or petroleum-based lubricating oils. For example, in the number 4 sample, the majority of the organics were C_{16} to C_{30} alkanes, a C_{22} substituted aromatic acid, and C_{26} and C_{32} branched chain aliphatic acids. For sample number 12, the majority were C_{18} to C_{26} alkanes, C_{32} and C_{26} branched chain aliphatic acids, and a C_{22} branched chain substituted aromatic chain. No polynuclears or organomercurys were found.

5.2 DISCUSSION

The explanation of what is occurring in the solid/liquid system over a period of ten washings is elusive. A straightforward correlation between the concentration of a metal in the solute versus either the quantity of metal in the dust or the pH changes of the solute after each washing is complicated by the possibility of numerous secondary reactions occurring once the meatls are extracted from the solids. Examples of secondary reactions include reprecipitation of metals as oxides, hydroxides, or even carbonates; oxidation of metals to a higher oxidation state, as in the case of Mn(II) and Fe(II); and trace element adsorption on and co-precipitation with a newly precipitated solid phase--e.g., MnO_2 and $Fe(OH)_3$ have relatively high ion-exchange capacities. Other secondary reactions are discussed in Section 7.2.1, Metal-Water Interaction.

The amount of the elements extracted from the solids is a very small percentage of the total amount available in the suspended residues except for antimony and in some cases cobalt (Table 30). The high percentages related to antimony can only be explained be differences in analysis methods and analysis error. There is no correlation between the quantity of cobalt extracted and the quantity in the solid phase (Figure 19); very little correlation for chromium, lead, manganese, nickel, selenium, or zinc (Figure 20); and some correlation for antimony and vanadium (Figure 21). This lack of correlation implies that dissolution was governed by inherent solubilities of the compounds.

The solubility of metals is known to be pH dependent, as illustrated in Figure 22 for zinc.[17] The concentration of zinc found in solution after one contact period and the pH are shown in Figure 23. If the solubility constraints for zinc oxide (or zinc hydroxide) from Figure 22 are plotted on the data in Figure 23, Figure 24 results. This correlates fairly well considering that equilibrium constants used in defining the solubility domain are for 25°C and zero ionic strength, solution conditions which are somewhat different than the actual experimental solutions.

Figure 25 shows the data points for soluble zinc as a function of pH after two contact periods. It is apparent that the extraction of zinc from the suspended dust particulates is determined by the solubility in zinc hydroxide which in turn is controlled by pH. Zinc solubilization is

TABLE 30. PERCENTAGE OF TOTAL METALS EXTRACTED FROM STEELMAKING FURNACE RESIDUES

	PERCENTAGE OF METAL EXTRACTED											
Residue Number	Antimony	Cadmium	Chromium	Cobalt	Lead	Manganese	Inorganic Mercury	Total Mercury	Nickel	Selenium	Vanadium	Zinc
1	194.4	N	0.004	10.6	0.9	2.2	---	---	0.2	N	---	19.5
2	72.7	---	0.03	46.1	0.02	0.4	---	---	0.9	N	---	0.001
3	144.3	---	0.01	7.4	0.04	0.003	---	---	---	N	---	0.01
8	N	---	---	19.0	---	0.009	---	---	---	N	---	0.1
14	14.8	N	---	2.6	0.3	0.1	---	---	0.2	N	---	1.0
17	86.7	2.9	---	11.1	0.04	0.2	---	---	0.7	N	---	0.5
4	56.0	N	0.08	0.4	0.02	0.001	---	---	0.0008	3.9	0.7	0.008
5	N	---	0.3	19.9	2.5	0.03	---	---	---	N	---	0.3
6	122.4	---	0.06	0.9	0.01	0.002	---	---	---	1.9	---	0.01
7	58.2	---	0.02	2.5	1.4	0.004	N	N	0.2	1.6	0.7	0.007
12	66.7	---	0.7	5.6	0.1	0.005	N	N	---	N	0.8	0.02
13	29.7	0.2	0.05	0.2	0.08	0.002	---	N	0.1	0.6	---	<0.03
18	37.7	N	0.03	12.1	0.09	0.1	N	N	0.08	N	0.9	0.04
9	N	---	---	1.8	2.4	0.01	---	---	---	N	---	0.06
10	347.6	---	0.06	30.7	1.7	0.001	---	---	---	N	0.6	0.01
11	N	N	---	1.3	3.8	0.02	---	---	>0.4	N	0.3	0.3
15	72.8	---	---	0.7	0.02	0.02	---	---	---	N	---	0.02
16	N	---	0.3	1.2	0.3	0.003	---	---	---	N	---	0.09

N = not reported in solid sample

--- = not found in extracted liquid

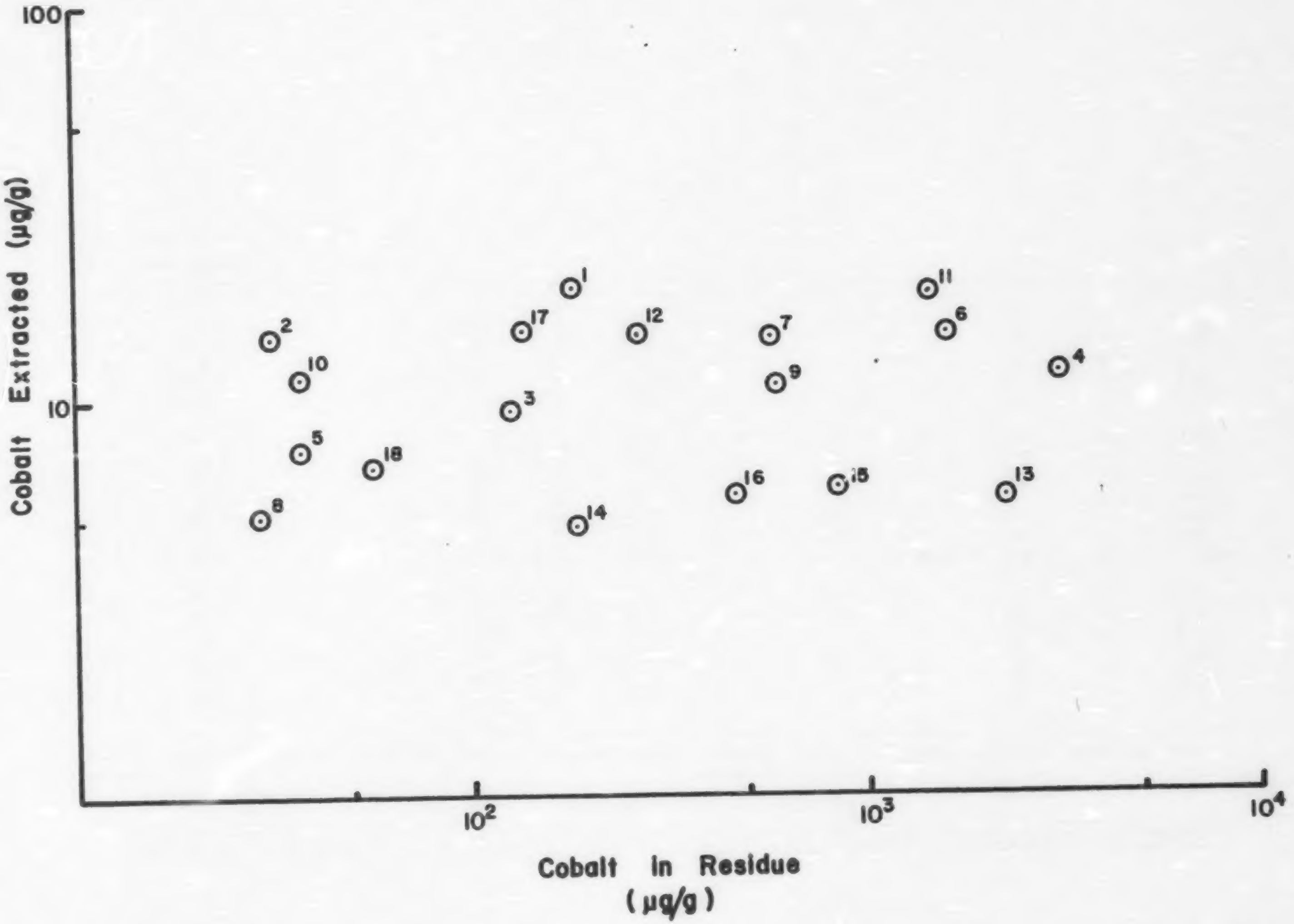


Figure 19. The relationship between the quantity of cobalt extracted and the quantity of cobalt in the residues.

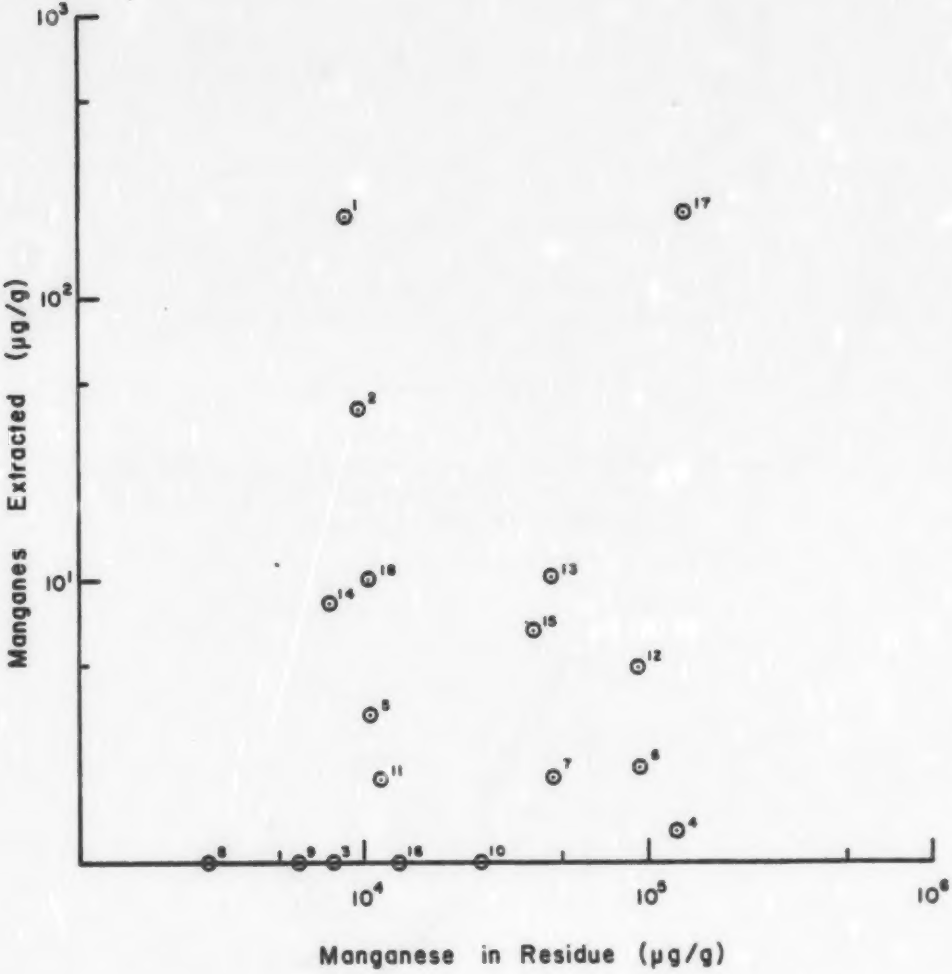


Figure 20. The relationship between the quantity of manganese extracted and the quantity of manganese in the residue.

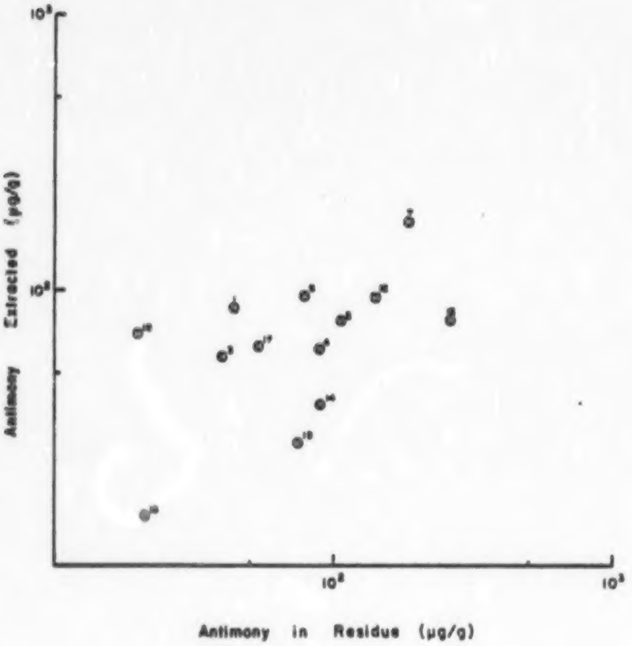


Figure 21. The relationship between the quantity of antimony extracted and the quantity of antimony in the residue.

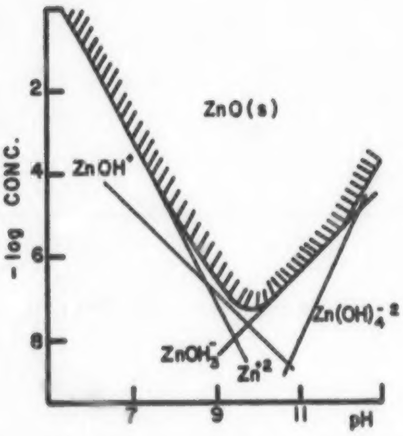


Figure 22. Solubility of zinc compounds.[19]

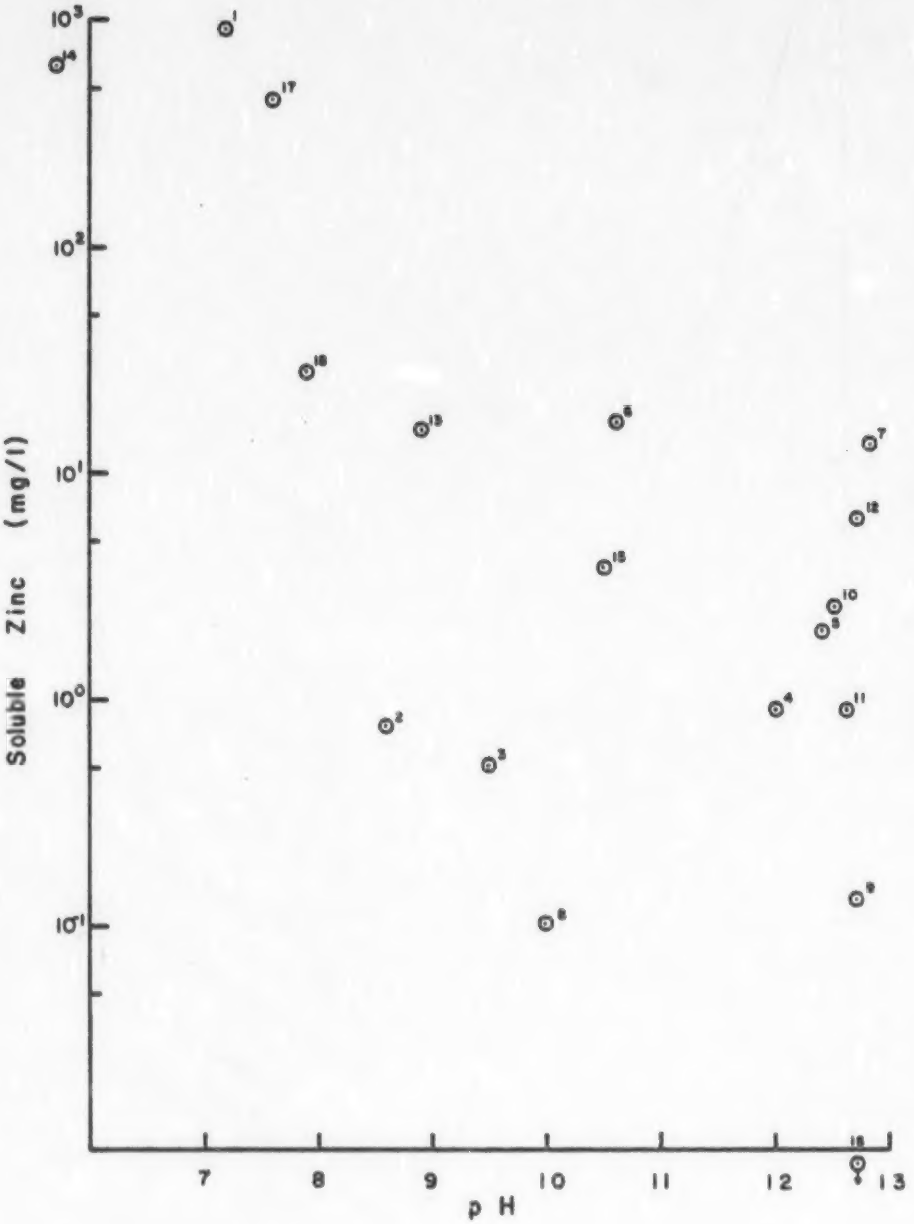


Figure 23. Relationship between soluble zinc and pH.

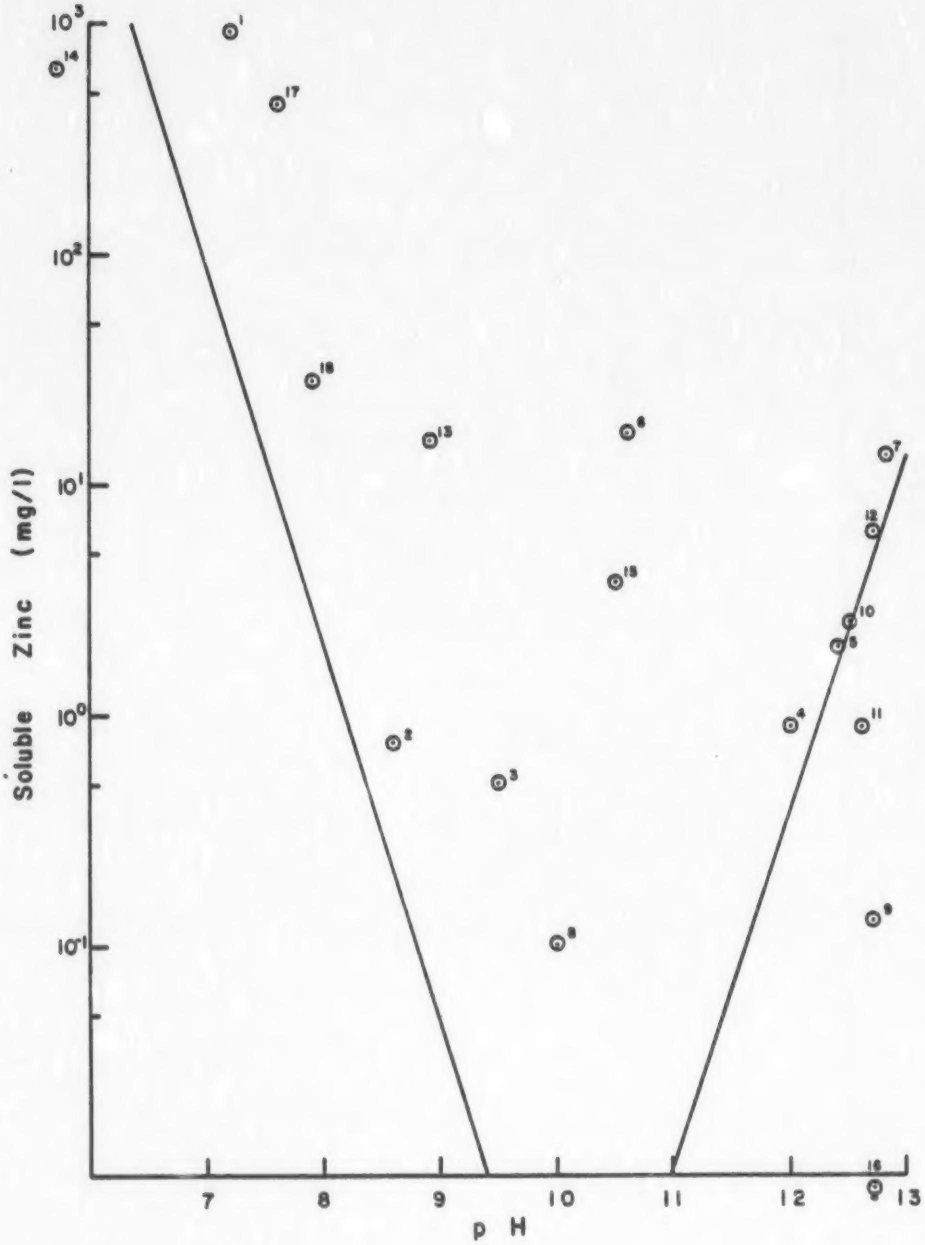


Figure 24. The relationship between soluble zinc and pH versus zinc solubility constraints.

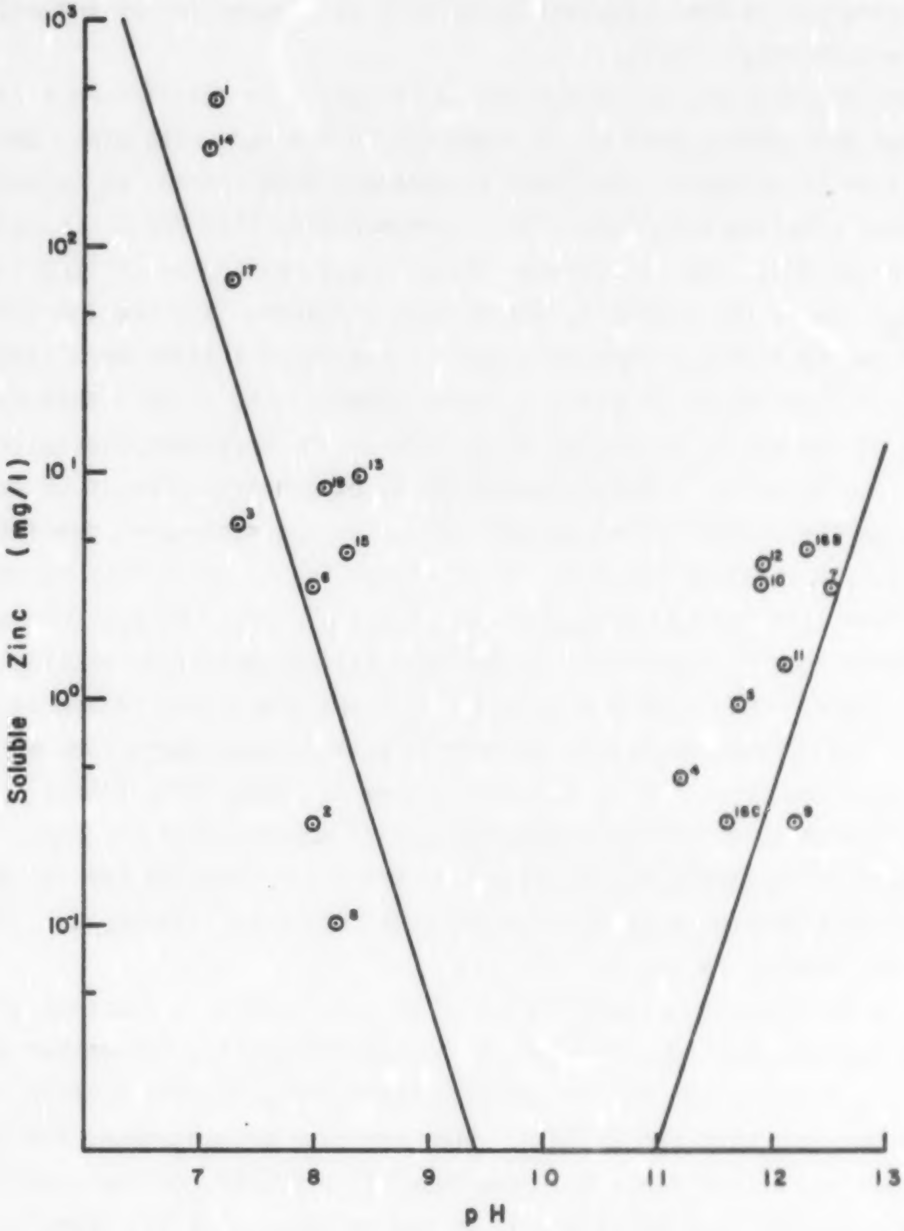


Figure 25. Relationships of soluble zinc as a function of pH after two contact periods versus solubility constraints.

appreciable in neutral solution, zinc being present as the free Zn^{2+} ion, and in strongly alkaline solutions where zinc is present in the anionic $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ forms.

Figure 26 shows the concentration of manganese in solution as a function of pH after one contact period. In contrast to the case with zinc, the concentration of manganese continues to decrease with increasing pH even in the strongly alkaline solutions. It is worth noting that Mn(II) is relatively soluble, while Mn(IV) is relatively insoluble and readily precipitates as solid MnO_2. It is reasonable to assume that manganese is extracted out of the dusts in the Mn(II) oxidation state. Since the solutions were shaken and exposed to oxygen in the atmosphere, it is plausible to surmise that some oxidation of the Mn(II) to Mn(IV) occurred with the resultant precipitation of MnO_2. The kinetics of Mn(II) oxidation by oxygen are strongly pH dependent,[20] and it is unlikely that there was much oxidation and subsequent precipitation below pH 9. In alkaline solutions Mn(II) oxidation is relatively rapid, and it would seem that the low manganese concentrations observed for all samples at pH greater than 11 can be attributed to Mn(II) oxidation to unsoluble MnO_2. In oxygen-containing solutions of high pH, the concentration of soluble Mn will be small, and $MnO_2(s)$ is the most stable (predominant) form of Mn. To illustrate the effect of pH further, Figure 27 shows three slices across Figure 20 for three different concentrations of manganese in the dust. The total amount of manganese extracted out of the solid phase by the ten washings is seen to be very much a function of pH with more metal leached out, in general, at lower pH values.

Figure 28 shows the concentration of soluble lead as a function of pH after one leaching period. At high pH, the dissolved lead concentration increases, presumably due to the species $Pb(OH)_3^-$ in a fashion similar to the situation with zinc and $Zn(OH)_3^-$. (For the case of manganese, the species $Mn(OH)_3^-$ does not appear since the manganese(II) probably gets oxidized and precipitates at the high pH values.) In the pH range 6 to 11, there is apparently little variation in lead concentration with pH. This is in contrast to the observations with zinc and manganese where the dissolved metal concentrations were appreciable below pH 9. The reason for this occurrence is not known, nor is it known why the concentration of dissolved cobalt is independent of pH after one contact period, as shown in Figure 29.

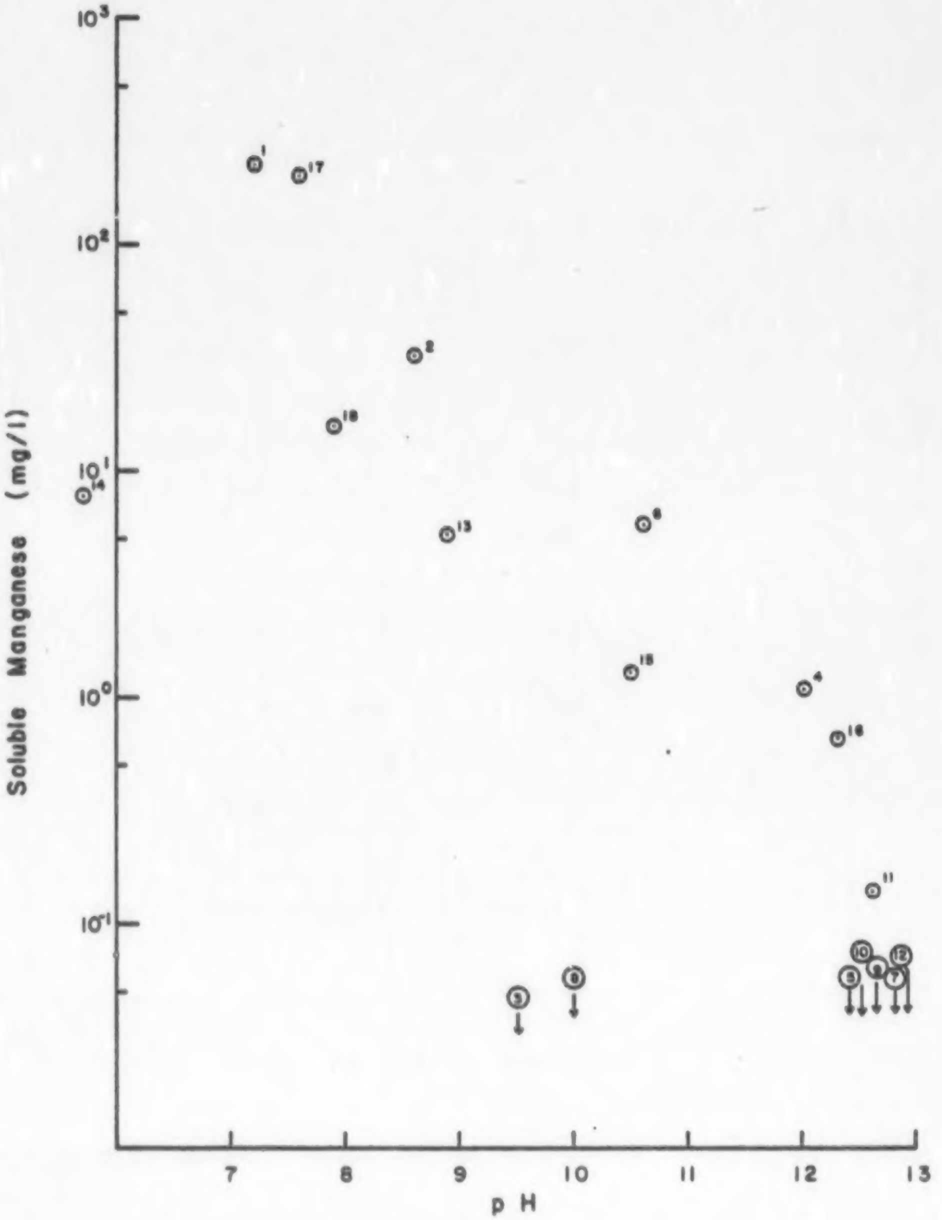


Figure 26. Relationships between soluble manganese and pH.

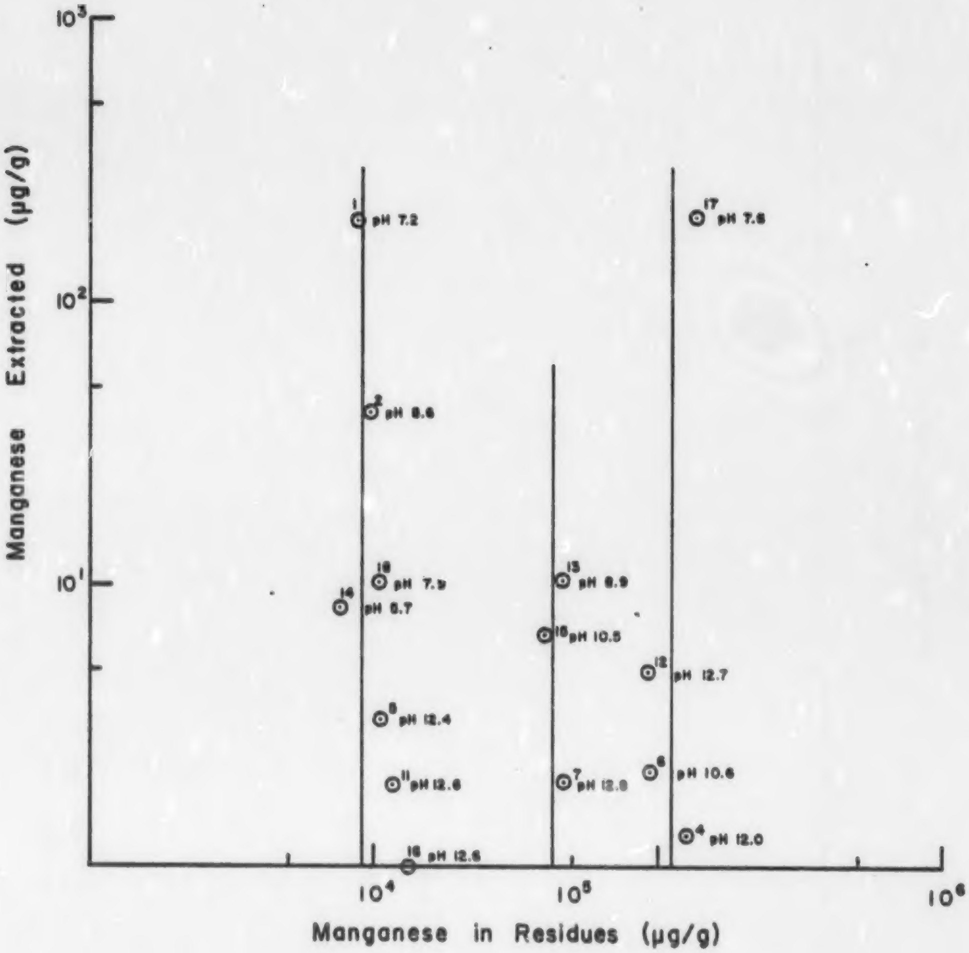


Figure 27. The effects of pH on the solubilization of manganese.

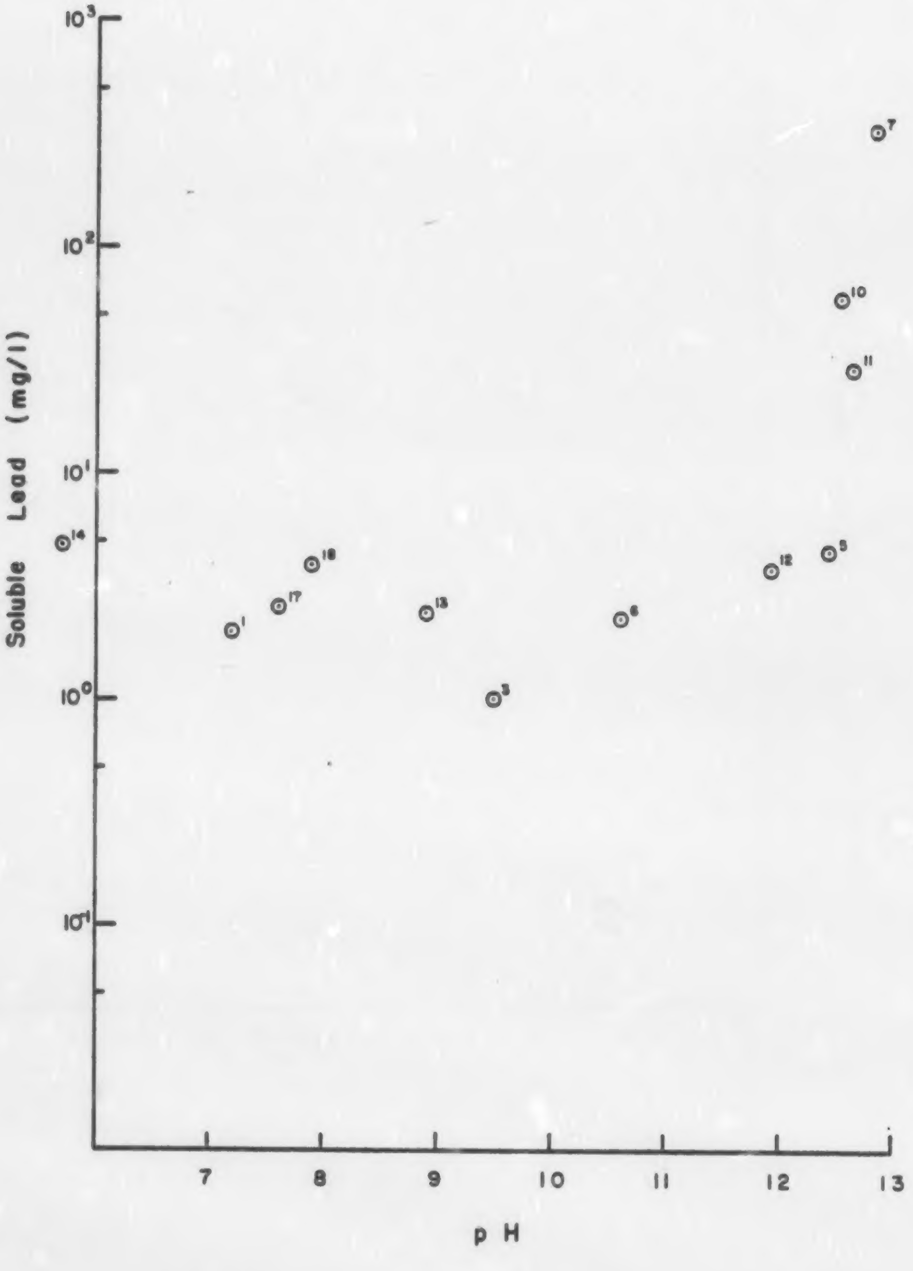


Figure 28. The relationship of soluble lead with pH.

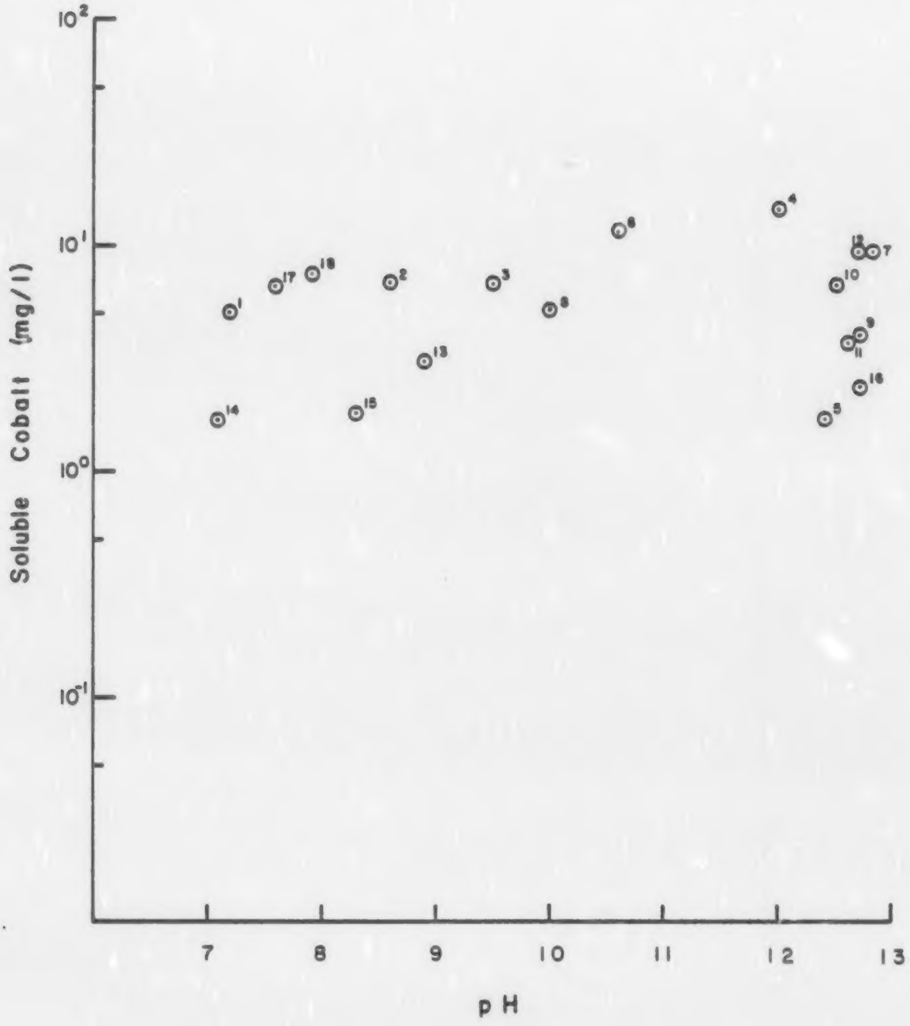


Figure 29. The relationship of soluble cobalt with pH.

Variable relationships between concentration and pH occur for many of the other elements. For inorganic mercury, total mercury, and vanadium, a lack of sufficient data points does not allow a trend analysis. For antimony, selenium, and nickel, concentrations after one contact period appear to be independent of pH as in the case of cobalt (Figure 29).

In the case of chromium, concentrations after one contact period appear to increase with increasing pH while they appear to decrease with increasing pH for cadmium (Figures 30 and 31). These results are consistent with solubility constraints.

It is apparent that the concentration of most trace metals leached from the dusts is dependent upon the pH of the solutions. Most of the dusts were alkaline in nature and caused the pH of the solutions in which they were suspended to increase to varying degrees. Since solution pH is such an important parameter defining trace metal behavior and solubility, it would be interesting to determine the basis for this alkaline behavior. If the metals are present in the dusts in the sulfate form, for example, their dissolution would have no effect on pH (e.g., $MnSO_4 \rightarrow Mn^{+2} + SO_4^{-2}$) but their subsequent precipitation would cause a decrease in pH (e.g., $Mn^{+2} + 2OH^- \rightarrow Mn(OH)_2(s)$). If the metals were present in the dusts as oxides and they were highly soluble metals, as for example calcium, their dissolution would cause the pH to increase (e.g., $CaO + H_2O \rightarrow Ca^{+2} + 2OH^-$). A plot of the calcium concentration in the dusts versus the pH resulting after one contact period showed only relatively low correlation between increasing pH and increasing calcium content in the dusts (Figure 32). The amount of Ca^{+2} actually extracted from the dusts was not measured. A better correlation of pH with leachable calcium may have resulted if Ca^{+2} was quantified.

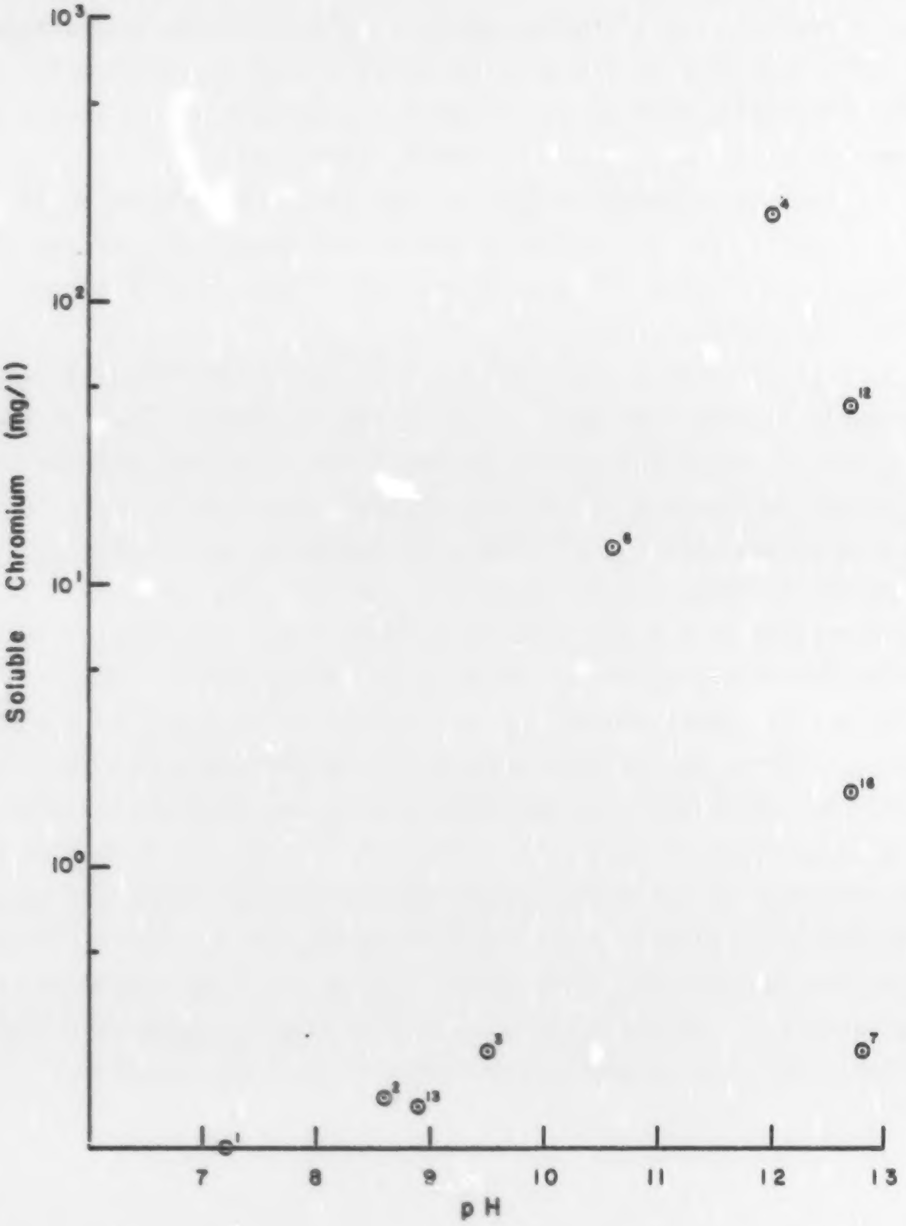


Figure 30. The relationship between soluble chromium and pH.

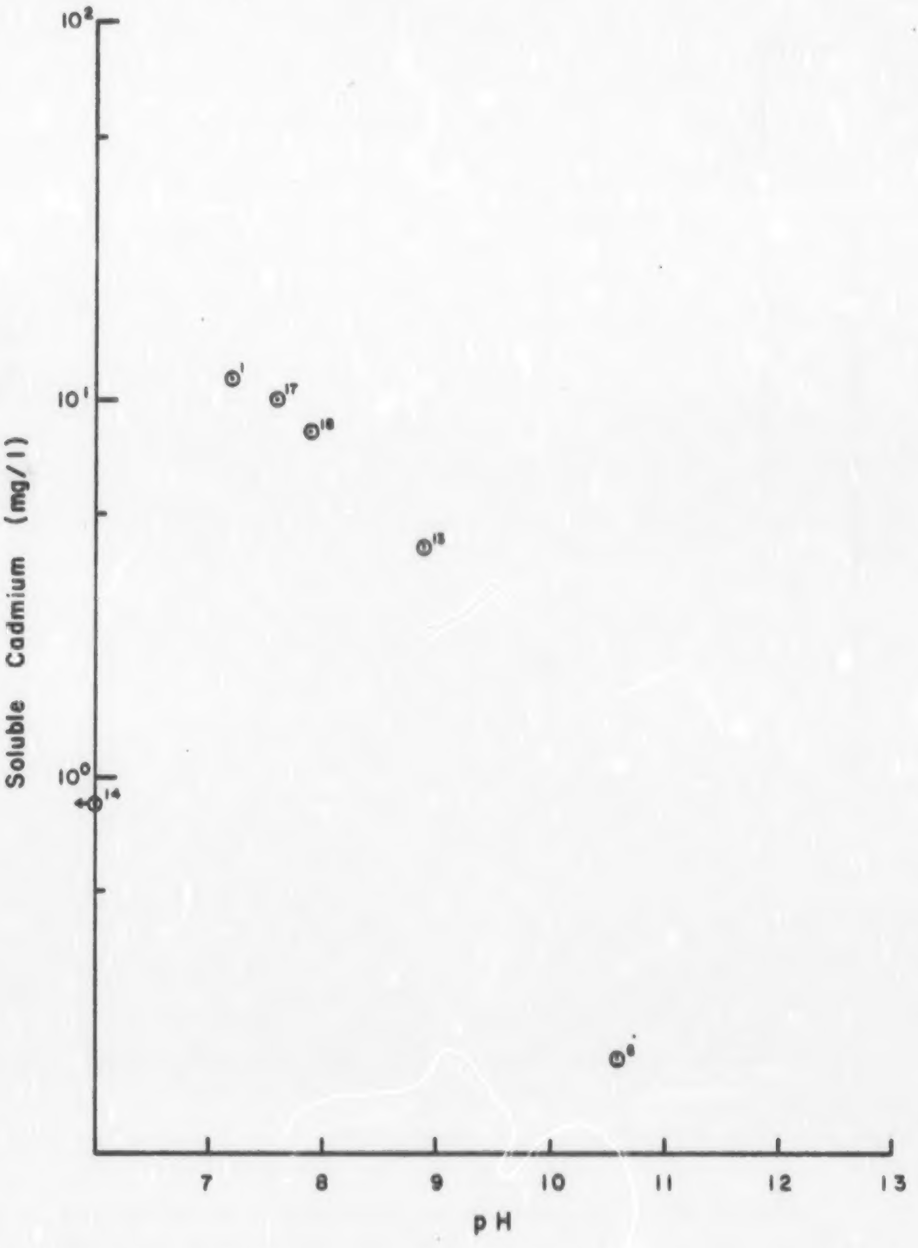


Figure 31. The relationship between soluble cadmium and pH.

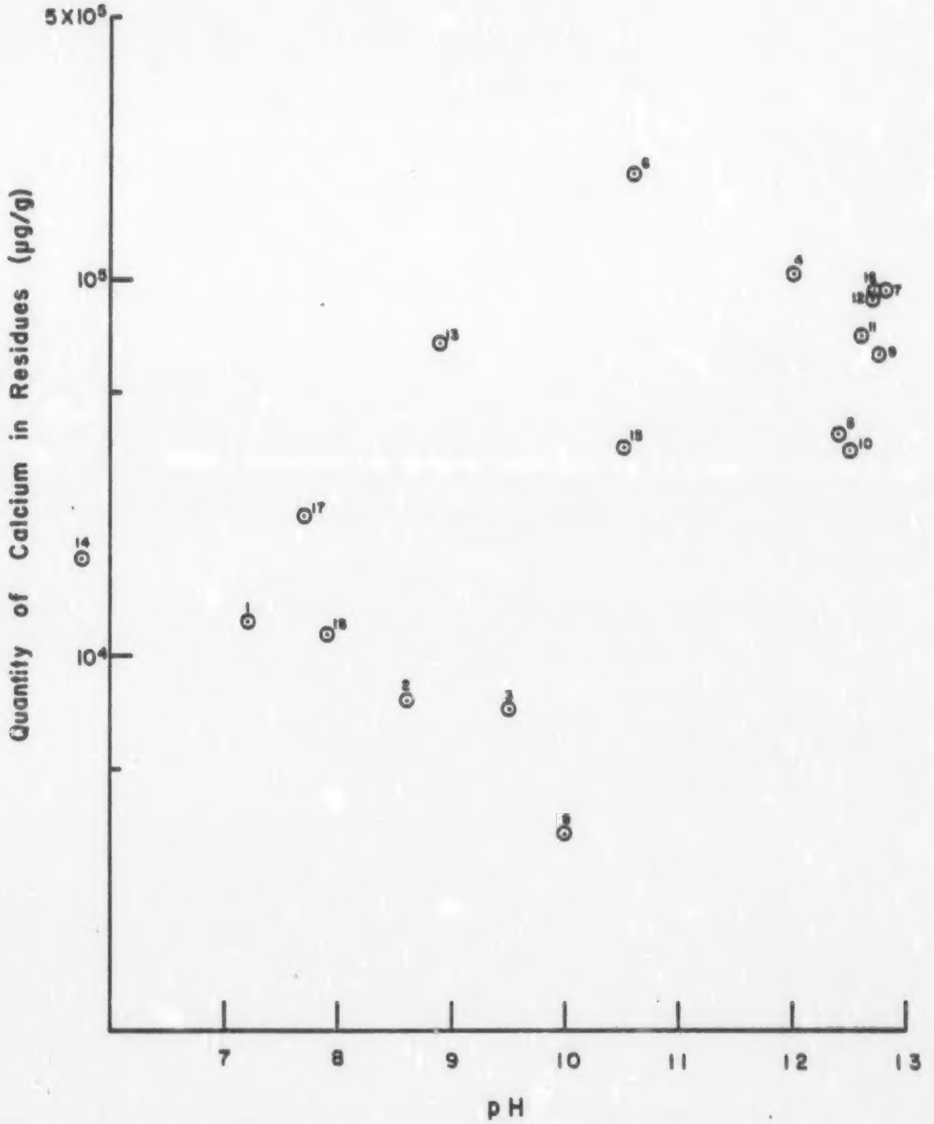


Figure 32. The relationship between the quantities of calcium in the residues and their effects on pH.

SECTION 6

HANDLING AND DISPOSAL OF STEELMAKING FURNACE RESIDUES

The handling and disposal of steelmaking residues are complicated by their physical and chemical properties. Generally, handling and disposal practices are those normally associated with solids and sludges from other types of operations.

6.1 HANDLING

The handling of dry steelmaking dusts presents environmental problems similar to those of other materials, i.e., wind blowing during transport and transfer. This dusting is compounded in the steel industry because of the fine nature of the residues. In some cases, the dry dusts are either mixed with water in a pug mill to form a semi-wet product or mixed with sludges from other iron and steel processes to facilitate handling.

Wet residues present a particular handling problem since prior to disposal, these residues are dewatered. Settling ponds or tanks are not effective because of the fine size of the suspended particles. Therefore, classifiers and thickeners followed by filters are used prior to settling. Additional operations may include the use of flocculants for settling and the adjustment of pH for acidity.

Along with fines, a coarse residue known as "sand" is recovered from the basic oxygen furnace control equipment. These sludges do not present any unusual problems and are usually separated in settling ponds or tanks, sometimes with the aid of rakes.

6.2 DISPOSAL

Essentially, three methods exist for the disposal of residues. The most commonly used method is heaping, either for direct disposal or for future use; the least used method is the utilization of the residues in other products; and the final method is recycling back into the process.

6.2.1 Waste Heaping

Waste heaping has been estimated to account for as much as 93 percent of these residues.[1] The heaping can occur either on-site or off-site. In most cases the residues are applied directly to the land although in some cases clay or tar linings are used to protect groundwater from waste leachings. In one instance, a Hypalon liner was used in a sludge lagoon.[1]

6.2.2 Residue Utilization

As mentioned previously, utilization of the residues to make other materials is not widespread. Some uses of these residues include paint pigments, paving, bricks, iron molds, base stone for road building, building fillers, wall and floor tiles, and "blueing" hydrangeas although markets are limited.[5,21]

6.2.3 Recycling

Recycling of steelmaking furnace residues is restricted because of physical and chemical properties of the residues. At the present time, approximately 7 to 12 percent of the total furnace residues are recycled.[1,6] The potential exists for recycling the residues to the blast furnace, the sintering operation, or to the steelmaking furnaces.

The chief restrictions on residue recycling to the blast furnaces are the physical fineness of the residues that causes them to be carried out of the furnace by the top gases unless the residues are agglomerated. The zinc and lead content of the residues cause problems with the refractory linings of the furnace and with the quality of the steel produced. In general, 0.2 percent zinc is considered to be an allowable maximum.[1]

Recycling to the sinter plant could become a viable alternative if certain difficulties are overcome. These include special handling and storage facilities to minimize the environmental problems associated with these operations, the careful and uniform proportionment of the residues into the sinter so as not to introduce an excessive amount that would weaken the sinter or destroy its quality, and the control of the amount of zinc-containing sinter entering the blast furnace.

The nature of the sintering process does not allow the removal of zinc from the residue prior to introduction into the blast furnace. Generally, the blast furnace can accept a maximum of 0.17 kg zinc per 1000 kg (0.33 pounds per ton) of molten iron without substantially affecting the equipment. This restriction necessitates carefully designed proportionment and feed controls. This is especially true if the burden materials also contain zinc.

Residues can also be recycled to the steelmaking furnaces without adversely affecting equipment, but with certain restrictions. This recycling can lead to a buildup of zinc that must be controlled by bleeding. The build-up of other substances such as lead, copper, and sulfur may prove deleterious to some grades of steel.

Other factors must be considered. The use of recycling introduces additional oxides into the furnace that absorb heat from the refining operation. In a BOF, for example, more molten iron would be required in the charge, and molten iron is in short supply in many plants. In addition, recycling equipment and the bleed systems must be designed to provide adequate environmental controls.

6.3 REGIONAL RECYCLING FACILITIES

The construction and operation of regional recycling facilities could be feasible in some cases depending on the type of process, the costs, and the geographical location. The most promising technology involves the mixing of the residues with a carbonaceous material, such as coking sludge, and pelletizing, drying, and heating at about 1093°C (2000°F) in a reducing atmosphere. This procedure results in the removal of approximately 90 percent of the lead and 90 to 95 percent of the zinc.[1] The resulting pellet can then be charged to either the blast or the electric arc furnace.

Several processes provide the technology necessary to produce suitable furnace feed pellets. Of these, the one that is in the most advanced stage of development is the Inland Steel-Heckett-Krupp Process. Others include:

--SL/RN Process, Steel Co. of Canada, Lurgi Gesellschaft fur Chemic and Huttenswessen, Republic Steel Corp. and National Lead Co.

--Kawaski Process, Kawaski Steel Co.

--Allis-Chalmers Process, Allis-Chalmers Mfg. Co.

--"Heat Fast" production process, Surface Combustion Co., Surfac Comb., Div. of Midland-Ross Corporation in collaboration with M. A. Hanna Co.

--Lummus Direct-Reduction Process, Lummus Co.

--ORCARB-Electric Furnace Process, Swindell-Dressler Corporation

--Arthur G. McKee & Co. Patent

--Wellman Engineering Co. Patent

--Bethlehem Ferro-Tech Process

--Bureau of Mines Process

--Inazaki Process (Japanese)

--Yawata Process

--Alan English Patent (No. 3,386,816)

--Sponge Iron Process of U.S. Steel Co., Geneva Works

A recycling system can be economically feasible when large amounts of residues are available for treatment, such as with regional recycling plants. The economics of a 363 x 10^6 kilograms per year (400,000 tons per year) plant are as follows:[1]

Capital Costs -- $18,000,000

This does not include the environmental costs or the costs for a 25-acre industrial site, which can be major items. For example, land costs in four possible regional sites are:

Site	Cost Range ($/acre)
Chicago	50,000 - 98,000
Pittsburgh	28,000 - 87,000
Philadelphia	50,000 - 131,000
Dallas	22,000 - 131,000

Charges in capital costs should follow a 0.60 to 0.65 size factor.

Operating Costs -- $34.00 per ton residue

Includes amortization, fuel, labor, transportation, and maintenance. Operating costs should follow a straight line function with 40 percent of costs constant and 60 percent increasing in direct proportion with the size decrease of the plant.

Revenues -- $40.00 per ton residue

Assuming equal revenue values from iron units (0.625 units, 85 to 90 percent iron per residue unit) and zinc units (0.05 units, 60 percent zinc per residue unit)

Net Return -- $6.00 per ton residue

This return provides for a write-off of 8 years. A conservative 10 year write-off is recommended due to uncertainties in the cost calculations.

Using the above assumptions and conditions, the economic break-even plant size would be approximately 281 x 10^6 kilograms per year (310,000 tons per year). Four steelmaking areas of the United States generate enough residues to support regional recycling plants. These include:

Chicago	544.3 x 10^6 kg/yr	(600,000 ton/yr)
Pittsburgh	435.5 x 10^6 kg/yr	(480,000 ton/yr)
Philadelphia	283.0 x 10^6 kg/yr	(312,000 ton/yr)
Southwest (Dallas)	239.5 x 10^6 kg/yr	(264,000 ton/yr)

The Philadelphia area may be doubtful because of a borderline net return potential and because of the widespread locations of the plants and the associated higher transportation costs. In the southwest area, residue quantities are low but both general economic conditions and the higher return on zinc units may provide favorable conditions.

SECTION 7

ASSESSMENT OF THE ENVIRONMENTAL IMPACT OF DISPOSAL PRACTICES

A major effort has been concentrated on controlling air pollutants from steelmaking furnaces to meet emission standards. While reducing the net emissions to the atmosphere, this control and the subsequent disposal of the collected residues has created environmental problems in itself due to the exposure of the residues to environmental elements. These problems are compounded by the large quantities of disposed residues and the multiple disposal sites (Table 31).

TABLE 31. ESTIMATES OF RESIDUE VOLUMES

	OPEN HEARTH		ELECTRIC		BASIC OXYGEN		
Year	Disposed Residues[1] (10^6 kg)	Volume[2] (10^3 m^3)	Disposed Residues[1] (10^6 kg)	Volume[3] (10^3 m^3)	Disposed Residues[1] (10^6 kg)	Volume[4] (10^3 m^3)	Total Volume (10^3 m^3)
1974	466.9	112.5	259.3	61.7	1065.6	252.6	426.8
1975	396.0	95.4	286.9	68.1	1161.4	275.2	438.7
1976	344.6	83.0	306.8	72.9	1226.7	290.7	446.6
1977	289.4	69.7	326.7	77.6	1293.3	306.5	453.8
1978	231.5	55.8	348.4	82.8	1361.3	322.6	461.2
1979	172.4	41.5	370.1	87.9	1431.7	339.3	468.7
1980	109.2	26.3	391.8	93.1	1502.3	356.0	475.4
1981	44.7	10.8	415.4	98.7	1574.2	373.0	482.5
1982	44.7	10.8	438.0	104.0	1583.3	375.2	490.0
1983	44.7	10.8	466.0	110.7	1589.9	376.8	498.3
1984	44.7	10.8	486.9	115.7	1596.4	378.3	504.8
1985	44.7	10.8	512.2	121.7	1601.6	379.5	512.0

[1] Disposed residues taken from Table 2.

[2] Based on an average bulk density of open hearth furnace residues of 4.15 x 10^3 kg/m^3 (see Table 8).

[3] Based on an average bulk density of electric furnace residues of 4.21 x 10^3 kg/m^3 (see Table 8).

[4] Based on an average bulk density of basic oxygen furnace residues of 4.22 x 10^3 kg/m^3 (see Table 8).

7.1 PATHWAYS FOR POLLUTANT MOVEMENT

The residues from steelmaking furnaces are normally discarded in aboveground waste piles, natural depressions or gullies, lagoons, or landfills. Pollutants from these residue piles can be dispersed into the enviroment by air transport, surface runoff, and subsurface migration. Estimates of the relative probabilities of potential environmental impacts by pollutants from the various disposal configurations are shown in Table 32.

TABLE 32. ESTIMATES OF POTENTIAL FOR ENVIRONMENTAL IMPACTS

	PATHWAY FOR POLLUTANT MOVEMENT		
Disposal Technique for Steel Furnace Dusts	Air Transport	Surface Runoff	Subsurface Migration
Heaps - permeable base	1	2	3
- impermeable base	1	1	5
Gullies and Natural Depressions			
- no dam	3	1	3
- dam with no overflow drain	3	3	1-2
- dam with overflow	3	2	2
- dam with drain	3	2	4
Lagoons	5	3	1
Landfill - lined	4-5	5	4-5
- unlined	4-5	5	2

Relative probability of transport: 1 - very acute; 2 - --; 3 - --; 4 - --; 5 - little movement potential--initial sampling sufficient.

7.1.1 Air Transport

Air transport of solid pollutants starts with entrainment of the particles. Entrainment can occur at each stage of the handling/disposal process. The potential for entrainment must be a function of the handling procedures of the plant, the characteristics of the residues (i.e., wet or dry, size, shape, etc.), transportation from the plant to the site, characteristics of the disposal site, and local climatic and topographic conditions.

Entrainment can begin at the collector transfer site and continue in the holding area, during the transfer to the disposal area, and in the disposal area. The emissions from each process are a function of existing conditions, the transfer mechanism, and the exposure to atmospheric processes. A quantification of these emissions is not readily available.

Entrainment of the dust particles arises from wind erosion. This commonly occurs during the transport of the dust to the disposal area by truck or by the action of the wind or traffic in the landfill area. The dust particles are picked up when the wind energy, expressed as the shear stress, at the ground exceeds a threshold value which is dependent upon the particles' size, shape, and density.[22] The shear stress, τ, is given by:

$$\tau = \rho {u_*}^2$$

where u_* is the velocity of the air at a characteristic distance above the ground dependent on the surface roughness, Z_0. The wind speed, u, at anemometer height Z, is related to u_* by the turbulent and thermal properties of the lower 10 meters of the atmosphere. The simplest relationship is:

$$u/u_* = 1/0.4 \cdot \ln(Z/Z_0).$$

Changes in roughness length from one location to another or at different locations at a site can make a substantial difference in the wind energy and, therefore, the emissions. The threshold velocity required to get a dust particle airborne should be linearly related to the density of the material and its aerodynamic cross-section presented to the wind. Some general relationships about threshold wind speed and particle pickup have been presented.[23] In this study, it was found that winds of 22.4 m/sec (50 mph) or more were required to set in motion particles as large as 2000 μm; particles between 1000 and 2000 μm could be transported under ideal conditions by wind speeds of 15.6 to 20.1 m/sec (35 to 45 mph); winds between 4.9 and 13.4 m/sec (11 and 30 mph) transport particles having sizes of 80 to 1000 μm; and as the particle diameter decreased below 80 μm, the threshold speed increased, so that particles of 2 μm diameter or less are not moved by winds below 22.4 m/sec (50 mph). The reversal of threshold speed is caused by the smaller grains being sheltered by the larger ones and increased adhesion of the small particles.

In the case of steelmaking residues where the majority of particle sizes are consistently below 80 μm, the effects of sheltering by larger particles would be negligable. However, the effect of the lack of sheltering is not quantifiable but is instrumental in the lowering of the threshold wind speed.

Surveys of particulate emissions from open coal piles showed a threshold wind speed of about 5.4 m/sec (12 mph) was needed to initiate emissions.[24] The emission rate was dependent upon an exponential power of the wind speed between 2.5 and 3.0, when the wind speed exceeded the threshold value.

Various characteristics of disposal sites can affect emissions from residue waste heaps. The most important characteristics are configuration, topographic location, and the moisture content of the residue. Also, the effect of time on heaps and the presence of plant life can reduce emissions.

The configuration of the residue heaps affects emmission rates. The above-ground dumped wastes in cone-shaped, tall piles or flat, fill-type mounds are more susceptible to wind erosion than waste landfills, lagoons, or gullies. The use of multiple small heaps rather than one large heap increases dusting because of the exposure of a larger surface area to the wind. In the case of a landfill residues can be transported by air if daily covering of the filled dust with a soil layer is not practiced. Lagoons or settling ponds should not present a dusting problem unless they are filled and evapcration causes the exposure of dried material to the wind. The disposal of residues in gullies or natural depressions would reduce their exposure to winds; however, wind movement can occur in small gullies, and a certain amount of wind channeling may occur if the gullies are large enough, thus producing wind erosion. This is a complex problem that is mostly site dependent.

Other factors that must be considered are the presence of tree buffers and siting on hillsides or in valleys.

The moisture content of the residues has an important influence on dusting. Laboratory data indicate that there is a decrease in the number of particles that become airborne as solid moisture increases.[22] The practice of disposing of steel residues in a wet or semi-wet form thus reduces the chance of dusting.

The effect of time on the surface of waste heaps could have an important influence on dusting. Older piles, exposed to weather effects over a longer period of time, may produce a crusty surface by agglomeration or binding due to water.

The presence of plant life on waste heaps can reduce dusting. Even with the high metals content of steelmaking residues, plants should eventually grow on older undisturbed heaps.

Once airborne, particle characteristics such as size, shape, and density play an important part in the transport of these pollutants from the piles. The size distributions for residues from steelmaking furnaces vary substantially for a given process and in many cases for residues from the same type of process.[6,8,10] The examination of dusts by electron microscopy revealed individual spherical iron particles in the size ranges of 0.04 to 62.09 μm, 0.02 to 35.00 μm, and 0.04 to 2.30 μm for electric, basic oxygen, and open hearth furnaces, respectively. These individual particles were frequently agglomerated into larger particles. In addition to the iron spheres, irregular carbon particles up to 900 μm long were found in all types of residues; irregular calcium particles up to 183 μm long in the electric and open hearth residues; and 3.50 to 13.90 μm cubes of titanium in one electric furnace residue.

Once these particles become airborne, some may remain for long periods. Studies of atmospheric dust have shown that the settling velocity of particles of 150 μm or greater is high enough to cause nearly instantaneous removal from the air, particles in the 1 to 150 μm size range fall out at a time dependent upon the inverse square of the radius, and particles smaller than 1 μm are nearly permanently airborne, having residence times of from 9 to 99 years.[22] The consideration of particle size ranges similar to those encountered by the electron microscopy examination (i.e., 0.01 to 10.00 μm) provides large terminal velocity variations. For a density of 10 g/cm^3, at atmospheric temperature and pressure, a 10 μm particle has a terminal velocity of 2.95 cm/sec allowing it to fall one meter in approximately 34 seconds. The 0.01 μm particle has a much smaller terminal velocity of 2.95×10^{-6} cm/sec. At this rate, the smaller particle will take more than one year to fall one meter.

Terminal velocities are also affected by both particle density and shape. Density has a nearly linear effect on terminal velocities while the effect of particle shape is essentially unknown due to both a lack of research and the variations in the measurement of equivalent particle size. Generally, the velocity relationships for spheres approximate (within ± 20 percent) those of irregularly shaped particles for $Re < 50$ when particle shapes are not extreme and particle size is measured as the diameter of equivalent spheres.[25]

7.1.2 Surface Runoff

Surface water runoff resulting from precipitation may transport suspended particles or dissolved material from the furnace dust waste deposition site. Heavy metal transport represents an immediate hazard to stream and reservoir water quality. Also, heavy metals may be transported from the original disposal site to surrounding land and vegetation.

The magnitude of transport by surface runoff and the relative importance of surface runoff compared to subsurface water movement depends largely upon the methods of disposal. Wastes buried in soil pits do not present a surface runoff problem, whereas waste piles exposed to precipitation are subject to particle dislodgement and transport as surface runoff. Also, any water that infiltrates the waste pile and confronts an impermeable base will be more likely to produce runoff containing dissolved waste material. Waste retained in gullies or depressions are impacted by runoff from upland portions of the watershed and this can greatly magnify the liquid contacting the waste in regions of moderate to high rainfall. Thus, the principles of runoff must be considered for direct runoff or water falling on the dust and for runoff aggravated by the dust storage location. In addition, overflow or drainage from lagoons, damed gullies or depressions may result in overland flow or channel flow of metal-laden water below the dam.

Factors which have been shown to affect erosivity of soil will most likely affect the erosivity of waste material. Therefore, one can hypothesize that the physical characteristics of the waste piles that will affect the erosivity and the water waste contact time include particle size and specific gravity, cohesive forces between particles, and shape of the pile (mainly slope length and percent).

The waste particles are smaller and heavier than most soil particles and relationships developed for predicting soil detachment by raindrops and soil transport by surface runoff would have to be utilized with extreme caution. The relationships between detachment and movement of soil particles by raindrops to the particle sizes are given by Table 33.

TABLE 33. RELATIONSHIPS BETWEEN DETACHMENT AND TRANSPORT OF SOIL PARTICLES BY RAIN

Particle	Particle Size (μm)	Relative Amount of Detachment and Transport (%)
Coarse Sand	590 - 840	30.0
Medium Sand	250 - 420	77.2
Fine Sand	175 - 250	100.0
Very Fine Sand	50 - 100	61.0
Silt	2 - 50	21.0

A higher percentage of fine sand was detached than coarse sand, and more coarse sand than silt. Most of the steel works waste particles are clay size (> 2 μm) but have specific gravities of 3 to 5 while soil mineral particles vary in specific gravity from about 2.5 to 2.75. It is difficult to say whether the metal particles would behave more like silt or fine sand. It was noted in one study that the smaller particles were compacted, the surface sealed, and a film of water developed at the surface which helped dissipate the energy of the falling raindrops and reduced the amount of particle detachment.[26]

The relative amounts of infiltration and surface runoff are dependent upon the compacting, crusting, aggregating, or agglomerating occurring at the surface. A crusted surface may produce sheet runoff which can reduce dislodgement of particles by reducing the amount of raindrop impact energy transferred to dust particles, but any sheet runoff also provides a means of transport for dislodged particles. A crusted surface may crack and induce gully or rill erosion. Thus, the erosion effect of crusting or compacting can best be determined by first carefully observing differences in pile surfaces and second, noting the relative movement of surface materials which has already occurred.

Other factors which will affect the surface nature of the pile are the initial texture and moisture content of the wastes when first piled and the surface changes due to wetting or drying. Dry particles may not wet easily without a mixing action to overcome fine particle cohesive forces: therefore, if the material is deposited dry, the raindrops may tend to bead and runoff.

The shape and distribution of piles will determine entrapment and surface storage of water which can result in less direct runoff and more infiltration. Greater side slopes increase water velocity and, therefore, erosion potential. Erosion on the pile will also depend on length of slope. The effect of degree and the length of slope have been combined into a generalized equation of predicting soil erosion under field conditions:

$$X = (C)(S)^{1.4}(L)^{1.6}$$

where X is the soil loss, S is the land slope in percent, L is the length of the slope and C is a constant that depends upon the infiltration rate, physical properties of the soil, intensity and duration of the rainfall, and other factors.[27] Thus, for identical pile characteristics, erosion will be a function of the characteristics of the precipitation. The dislodging of soil particles by raindrops to several rainfall characteristics[28] is related by

$$\text{Dislodging} = f[\text{precipitation intensity} \times \text{time} \times \frac{\text{drop mass}}{\text{drop cross-section}} \times (\text{drop velocity})^2].$$

This indicates that climatic conditions of the disposal site will influence surface runoff and erosion because of different rainfall amounts and patterns of intensity and drop kinetic energy. In addition, the relative amounts of precipitation and evaporation vary with regions causing some regions to have moisture excess. This normally means more surface runoff and overflow of reservoirs (including waste lagoons). These climatic factors can be assessed from available weather data.

Once the particles have been detached and transported to the base of the pile, any further transport will depend largely upon the runoff and erosion potential of the surrounding area. In order to transport the steelworks waste particles, certain minimum or threshold velocities will have to be obtained. An equation for threshold velocity of unigranular materials ranging in diameter from 0.35 to 5.7 mm and in specific gravity from 1.83 to 2.64 has been developed.[29] This equation is

$$V_t = 0.5\ d^{4/9}\ (G-1)^{1/2}$$

where V_t is the threshold velocity (ft/sec), d is the particle diameter (mm), and G is the specific gravity. Using $G = 5$ and $d = .002$ mm, the predicted V_t is 0.02 m/sec (0.06 ft/sec). Overland flow velocity is typically 0.30 to 0.61 m/sec (1 to 2 ft/sec); therefore, this equation would predict that these waste particles would be transported. However, caution must be used since particles of this size and density were not used in developing the equation.

Using previously developed equations for predicting soil detachment and transport, it can be proposed that most of the same factors such as rainfall intensity, raindrop kinetic energy, slope, and slope length of pile will influence transport of these waste particles. Factors such as surface crusting, infiltration, and solubility of wastes can potentially have a large effect. While snow melt is not covered here, it certainly would be a contributory factor in snow regions. Relatively little is known of this runoff mode and specific experimental consideration would be necessary to determine these effects. Therefore, the initial steps in determining the environmental impact from the steelworks waste piles should probably be to observe the waste piles to detect runoff and erosion, and to sample water and sediment that may indicate transport of the waste from the deposition site.

7.1.3 Subsurface Migration

A certain amount of water that comes in contact with steel mill furnace dusts will leave the area as subsurface water. This water may move vertically into the groundwater or laterally to finally enter surface waters such as a stream or lake. Waters may also move laterally to a recharge area, then vertically to a groundwater aquifer. It is assumed in this section that these waters may carry materials that are toxic or at least potentially harmful. Several examples of groundwater contamination due to the movement of chromium from disposal sites for electroplating wastes have been documented.[30] While there are probably many other references to groundwater contamination by metals that are contained in mill waste, no attempt to perform an exhaustive search of the literature has been made. Instead, the general conditions and factors affecting the subsurface movement of any materials from a disposal site and methods that could be used to detect such movement are discussed. The existence of toxic materials in the mill wastes, their solubility in water, and the extent to which they will be tied up by the soil particles are covered in the following sections of the report.

It seems clear that any subsurface movement of pollutant materials in soil will take place in soluble form. The subsurface movement of particulate matter in soil beyond a centimeter or two is almost certain to be negligible. Experiments with soils have shown negligible translocation of even clay sized particles

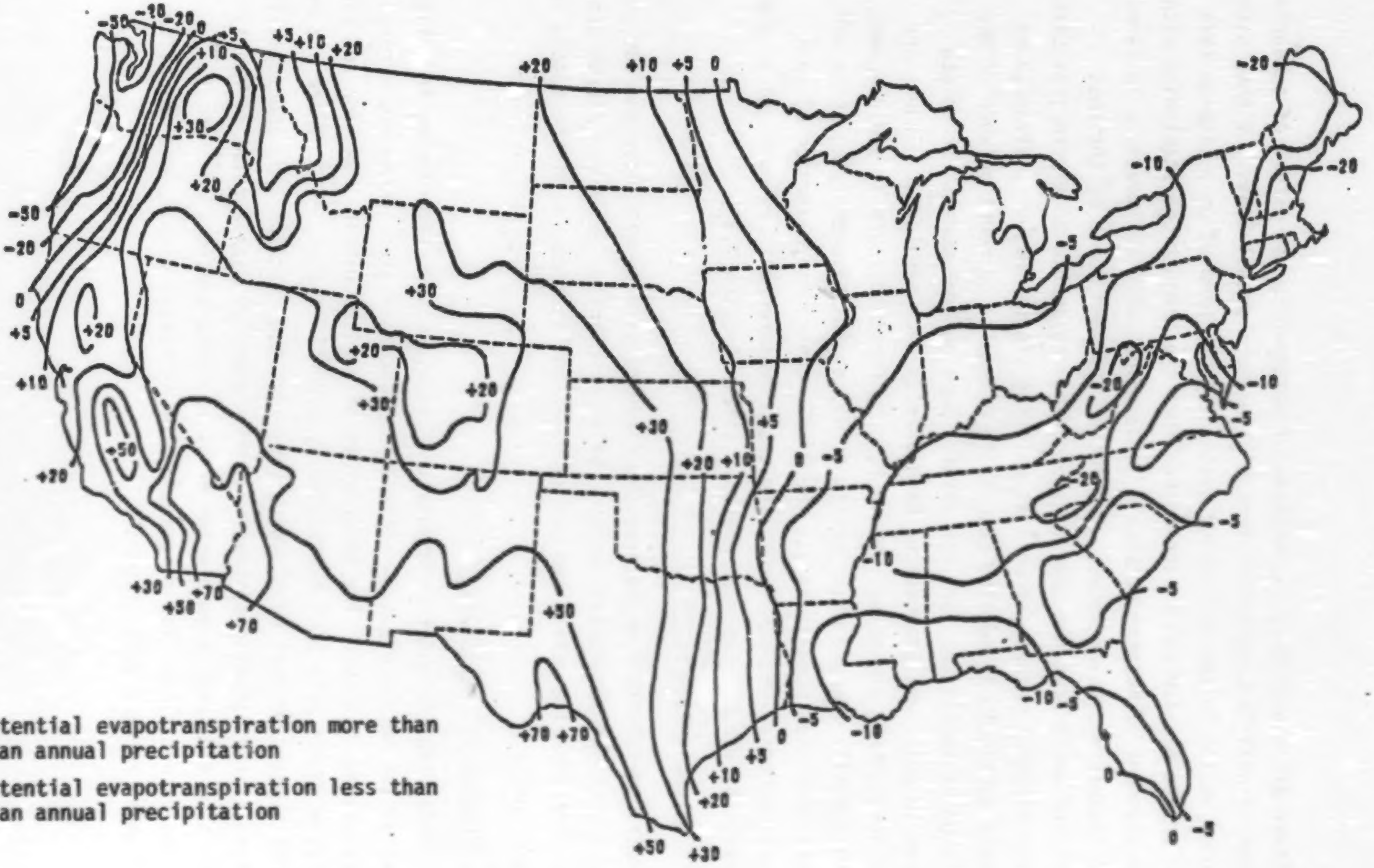
(< 2 μm) for short-term experiments.[31] Many of the materials present in mill wastes have been shown to be soluble in water and can thus move with the water through the soil profile and beyond.

The directions and rate of movement of pollutant-laden waters from mill waste disposal sites will depend on several factors. These include factors that are dependent on the pollutant being transferred, site factors, soil factors, and climatological factors. One important factor in the first category is sorption of the pollutants on the soil particles. Some materials will be tightly "sorbed" and will not move through the soil while others such as the Cl^- ion move freely with the soil water. Obviously those materials that are held tightly will pose less of an immediate problem than those which move more readily. Possible chemical or biochemical reactions which change the form of "sorbed" ions and increase their mobility should be considered in this regard.

Site factors include slope, distance to groundwater, site elevation, and surrounding streams, lakes, and wells (both present and future). The characteristics of the disposal site (piles, landfills, lagoon, etc.) are also included here and will be discussed in detail in a later section of this report (Section 7.3). The site factors determine the direction and magnitude of prevailing hydraulic gradients and thus the movement of pollutant-laden waters.

Soil factors include those soil properties that govern the rate of subsurface water movement and the dispersion of solutes as the water moves. These include the hydraulic conductivity (both saturated and unsaturated), the dispersion coefficient which is dependent on both the soil and the solute, lenses, layering, and the depth and thickness of restricting layers.

Climatological factors are of obvious importance since the pollutants are carried by water. In a high rainfall area deep seepage to groundwater aquifers is more likely than in an area where potential evaporation exceeds rainfall (Figure 33). Thus subsurface movement of pollutant materials will be slower in drier regions, and pollutants will be less likely to be flushed out of the soil-water system by infiltrating waters.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+ Potential evapotranspiration more than mean annual precipitation

- Potential evapotranspiration less than mean annual precipitation

Figure 33. Potential evapotranspiration vs. mean annual precipitation (inches).

There are essentially two methods of determining the extent of subsurface movement of pollutant materials from mill waste disposal areas. Either distribution of wastes in the soil-water system can be measured on a site-by-site basis, or the problem can be approached from the theoretical standpoint with the development of methods or models to describe pollutant movement in terms of the factors discussed above. The latter approach would be the most general and would have the advantage of being applicable to alternative sites and land disposal methods as well as existing sites. However, it would be extremely difficult to develop and verify a prediction model because of the wide range of conditions that now exist. Some general models for solute movement in soils and groundwater have already been developed. Others are in the development processes. However, as a first approach it would appear best to actually measure distribution of wastes in the underlying soils and aquifers near the sites to assess the likely environmental impact of such disposal methods. Methods for making these measurements are outlined in the discussion of various types of disposal sites (Section 7.3).

7.2 POLLUTANT INTERACTIONS

Metal pollutants removed from the disposal site by water systems can interact with the intercepted water, soils, or plants. Soils and plants can also act as sinks for the metals and can serve as the introducers of the metals into the food chain.

7.2.1 Metal-Water Interaction

Metal ions in water undergo extensive hydrolysis and complex formations. Several of the metals exist in different oxidation states in the redox range of most aqueous systems. The pH-E_h plots of various metals like iron and zinc in solution phase have been elucidated by several studies.[32,33] There are many chemical species of each metal which vary with the reaction (pH) and redox (E_h) condition of the acquatic systems. At pH's near 7.0 with a redox of nearly 200 mV, zinc and iron in pure water exist as ionic species, Zn^{++} and Fe^{++}. Thus, the potential for ion movement can be increased with E_h and pH shifts likely under furnace dust disposal.

Metal ions react and sorb with the organic molecules and may result in formation of soluble chelates such as iron-humate and insoluble complexes such as calcium-humate. Soluble metal ions and chelates are mobile and constitute the most common dispersion route of metals with potential impact on surface as well as groundwater.

Under alkaline (pH 10-12) and oxidizing conditions, such as the steel mill dust, certain metals transform to their oxidized state such as $Fe(OH_3)$, Fe_2O_3, MnO_2, etc. Kinetically, oxidation of Mn^{2+} is relatively slow. Therefore, Mn^{2+} tends to persist longer in aerated waters than does Fe^{2+}. These oxidized states of many metals may eventually lead to formation of colloids and precipitates under high ionic strength and osmotic concentrations. Under reducing conditions, metal ions tend to transform to lower oxidation states which are more soluble and stable under acid conditions.

Significant amounts of antimony, mercury, cobalt, lead, zinc, chromium, selenium, and manganese solubilize in water washings of airborne dust from steel mills (Table 34).

TABLE 34. WATER SOLUBILITY OF METALS FROM THE AIRBORNE DUST OF 18 STEEL MILLS

	CUMULATIVE CONCENTRATON (ppm) IN 10 WASHINGS		
Element	Maximum	Minimum	Remark
Pb	1437.9	2.0	
Zn	1145.3	0.9	
Co	410.0	4.0	
Cr	253.9	0.1	
Mn	228.1	0.2	
Sb	184.9	22.2	
Se	173.7	0.9	
Hg	136.1	10.0	Only Electric Furnaces
Cd	13.7	1.3	
V	6.5	1.1	
Ni	1.9	0.5	

Considerably greater amounts of metals may be solubilized in acidic waters or waters with organic and inorganic impurities as might be encountered at a variety of disposal sites especially when mixed with other wastes. The presence of mercury in water extract of metallic dust from electric process steel mills indicates its soluble form as ions Hg^+, Hg^{++}. Mercury, lead, and zinc appear to be the most hazardous of all elements in metallic dust from environmental considerations of surface water pollution.

7.2.2 Metal-Soil Interactions

The soil matrix consists of mineral particles in clay (< 2 μ), silt (2-50 μ) and sand (> 50 μ) size fractions; organic matter at varying stages of decomposition; living microorganisms; water with soluble ions and complexes; and air. All these soil components interact with metals reaching the solid system in various forms and amounts.

Chemically the airborne steel mill dust is abundant in iron, zinc, chromium, calcium, manganese, and/or lead in contrast to soils, the mineral fraction of which is made up of alumino-silicates (Table 35). Metallic dusts from 18 different steel mills possessed a wide range of elements in varying proportions in as yet undetermined chemical combination or form.

Some of the salient interactions that metals undergo in soils are outlined below.

Ion exchange reactions and adsorption--Soils with high cation exchange capacity such as clay and organic soils would absorb and retain considerable amounts of metallic ions. The order of adsorption of metal ions on soil colloids is approximately $Cu>Pb>Ni>Co>Zn>Ba>Rb>Sr>Ca>Mg>Na$. Thus constituents of furnace dust can be screened using the least absorbed species.

Metal fixation reactions--Chemical reactions in which metal ions bind to the soil inorganic fraction irreversibly or substitute isomorphically for other ions of similar radii from mineral structure, do occur and are an essential feature of chemical weathering phenomena and clay formation:

$$\underset{\text{(soluble)}}{M^{2+}} \rightarrow \underset{\text{(exchangeable)}}{M-X} \rightarrow \underset{\text{(fixed)}}{(XMX)} .$$

TABLE 35. ELEMENTAL COMPOSITION OF STEEL MILL AIRBORNE DUST AND OF A MINERAL SOIL

	METALLIC DUST %		
Element	Maximum	Minimum	Soil, %
Iron, Fe	> 50	31	4.0
Zinc, Zn	> 32.5	0.08	0.02
Chromium, Cr	18.1	0.018	0.01
Calcium, Ca	14.2	0.34	3.6
Manganese, Mn	13.2	0.288	0.1
Lead, Pb	10.86	0.011	0.01
Silicon, Si	6.7	0.44	27.7
Potassium, K	5.4	0.02	2.6
Nickel, Ni	4.64	0.004	0.004
Magnesium, Mg	4.5	0.36	2.1
Sodium, Na	3.1	0.03	2.8
Chloride, Cl	1.6	0.03	0.01
Molybdenum, Mo	0.685	0.005	tr*
Copper, Cu	0.57	0.014	0.01
Aluminum, Al	0.45	0.007	8.1
Phosphorus, P	0.35	0.04	0.07
Cobalt, Co	0.31	0.003	0.001
Selenium, Se	0.244	0.016	tr*
Tin, Sn	0.192	0.002	tr*
Scandium, Sc	0.11	tr*	tr*
Cadmium, Cd	0.104	0.035	tr*
Arsenic, As	0.055	0.003	0.002
Vanadium, V	0.053	0.008	0.01
Carbon, C	0.03	tr*	2.0
Antimony, Sb	0.026	0.002	0.001
Silver, Ag	0.013	0.002	tr*

*tr refers to trace, < 10 ppm in total sample.

Manganese and aluminum, for example, may substitute for iron and silicon, respectively, in silicate clay structures, creating a permanent change. Thus, metal ions are fixed permanently and irreversibly. This pathway represents a desirable route since, in this form, metals become unavailable for movement or uptake.

Precipitation--Reaction of metal cations with anions like phosphate carbonate, and sulfide leads to formation of insoluble precipitates with extremely low solubility products. Lead in solution may react with phosphates and molybdates, forming very insoluble precipitates. The metallic colloid particles may aggregate and the precipitate in high-salt waters by forces of coagulation and flocculation. The order of insolubility of various metallic sulfides is Hg>Cu>Sn>Pb>Ni>Co>Cd>Zn>Fe>Mn>Mg>Ca.

Chelation--Coordinate bonding between a metal ion and chelating ligand in soil may form complexes of varying solubility constants. The soluble metal complexes may be anionic, cationic, or without any charge dependeng on the pH of the media. Formation of low molecular weight soluble metal-organic complexes increases the mobility of metals, and the chances of surface and groundwater contamination are greatly increased.

The insoluble chelates, on the other hand, irreversibly bind and prevent the metal pollution of water. The order of stable chelate formation of various metals in Hg>Cu>Ni>Pb>Co>Zn>Cd>Fe>Mn>Zn>Mg>Ca.

Oxidation-reduction--Most metallic ions undergo change in their oxidation state depending on the redox status of soil. Soil redox is strongly influenced by moisture aeration relationships, wetting and drying, and nature and extent of microbial activity. Certain metals under aerobic conditions oxidize quickly and may form metallic oxides like Fe_2O_3, MnO_2, etc. These transformations may be directly mediated by soil microorganizms. The oxidized state of metal ions is virtually immobile, thereby reducing the probability of water pollution. Reduced forms of metal ions are soluble and more subject to move with leaching water than are oxidized forms.

Methylation-demethylation--Certain metals like mercury, arsenic, selenium, and cadmium are biochemically methylated and demethylated in soil and sediment systems. Methylated metal species are more mobile and toxic as contaminants than elemental or ionic forms. Methyl-mercury can move with water flow to plant roots or to streams where it can enter the food chain or may be enzymatically demethylated into elemental forms.

Mineralization-immobilization--Certain metal ions such as iron, manganese, copper, zinc, calcium, magnesium, potassium and molybdenum are essential in trace amounts to various microbiological functions and synthesis of biomass. Effects of different nonessential metals on soil microbes have not been well studied. Silver and mercury are most toxic followed by cadmium, nickel, lead, chromium, and barium.

7.2.3 Metal-Plant Interactions

Plants require 16 elements for growth and essential metabolic functions. Of these, iron, copper, zinc, manganese, calcium, magnesium, potassium, molybdenum, cobalt, phosphorous, and chlorine are present in the metallic dust. Non-essential elements present in the dust are arsenic, silver, cerium, cadmium, chromium, silicon, lead, aluminum, barium, sodium, nickel, vanadium, tin, scandium, yttrium, zinc, niobium, and antimony. Very little is known about the interaction of non-esential metal elements with plants. Metal ions may reach the foliage of plants in the form of dust or dirt blown by wind. In solution phase, dissolved metal ions or complexes may reach the plant roots by root interception or contact (e.g., Hg, Cu, Ni, etc.), mass flow of solute metal with water (e.g., Fe, Ca, Mg, Al, etc.), and diffusion of metal ions in accord with an ion activity gradient (e.g., Zn, Mn, etc.).

Once the metal ions and complexes reach the root surface, they may compete with other ions for carrier site uptake. Plant species differ markedly in accumulation of and requirement for different metals. Entry of metals into plant roots and further translocation to tops may be categorized into the following modes:

1. Metals like iron form strong, slowly exchangeable chelates at the root epidermis and move intact from epidermis to leaves.
2. Metals like copper and chromium form similar chelates as iron with little or no ability of chelate to enter the xylem.
3. Metals like zinc and manganese remain soluble in the chelator pool and the chelators hold very little control on their movement.
4. Metals like lead and aluminum may be precipitated by phosphate or may form a mixed chelate precipitate with the ion exchange surfaces in the root.

5. Metals like mercury and nickel may bind to very stable, slowly exchanging macromolecules or ion exchange surfaces and not be soluble enough to reach the xylen parechyma cells.

Increased mobility of metal ions by solubilization or formation of soluble metal-chelates also increases their availability to plants.

Above a certain critical concentration or accumulation threshold level, the metal may exert a toxic influence on plants and animals. An attempt to classify the metals based on their 50 percent lethal dose has been made and their modes of toxic effects have been discussed.[34] The order of problem metal toxicity to oats is Ni>Cu>Co>Zn>Mn, whereas, to sugar beet it is Co>Cu>Zn>Ni>Mn. Some of the metals like Cd and Se may accumulate in plants at levels that are lethal for animal and human consumption. Plants may exert influence on solubility and transformation of metals in the rhizosphere. Initially, accumulation of large amounts of metals from steel mill wastes may prohibit vegetation growth at the dumping site. Sooner or later, metal-resistant flora and fauna would evolve with ecotypes adapting to metal rich environments. Plant species vary in evolving ecotypes tolerant to one metal and not to the other.

7.3 SPECIFIC DISPOSAL CASES

This section examines specific disposal cases for steelmaking residues. The potential for environmental effects and methods for sampling and evaluation are presented.

7.3.1 Heaps

Heaps are the most commonly used method of residue disposal. Most heaps have permeable bases although some heaps with impermeable base "liners" do exist. Infiltrating water can carry waste material below the soil surface and from there to either groundwater (Figure 34) or laterally to surface waters (Figure 35). Lateral movement is the critical element when restricting layers are at a shallow depth, if the heap is located on an incline or in a position where water is moving laterally from other surfaces, and in the case of heaps with impermeable bases where no downward movement exists.

The magnitude of this problem will be affected somewhat by infiltration and seepage through the waste material. If the material is a very fine dust, it

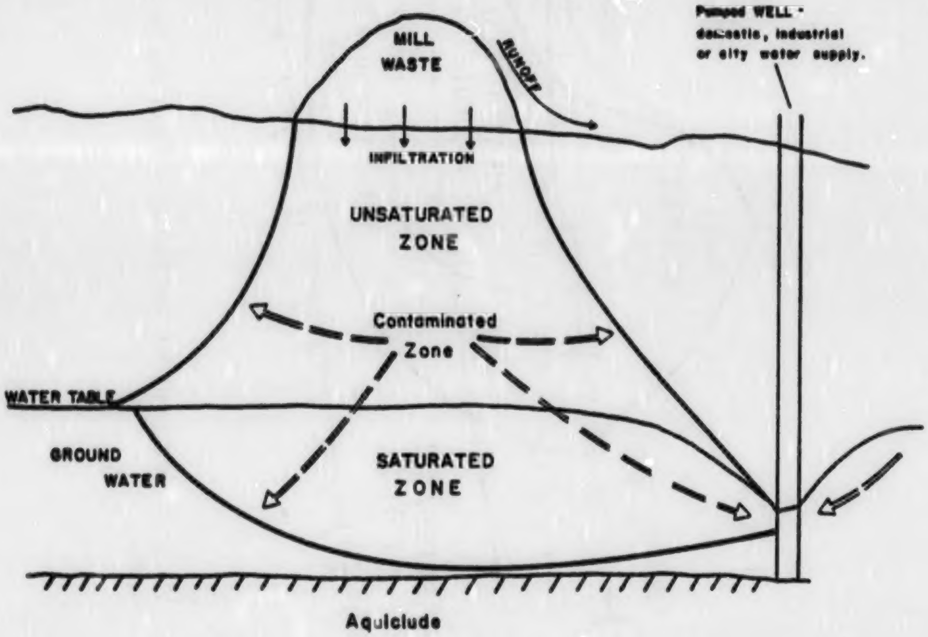
MILL WASTE
RUNOFF
Pumped WELL - domestic, industrial or city water supply.
INFILTRATION
UNSATURATED ZONE
Contaminated Zone
WATER TABLE
GROUND WATER
SATURATED ZONE
Aquiclude

Figure 34. Migration of pollutants to groundwater.

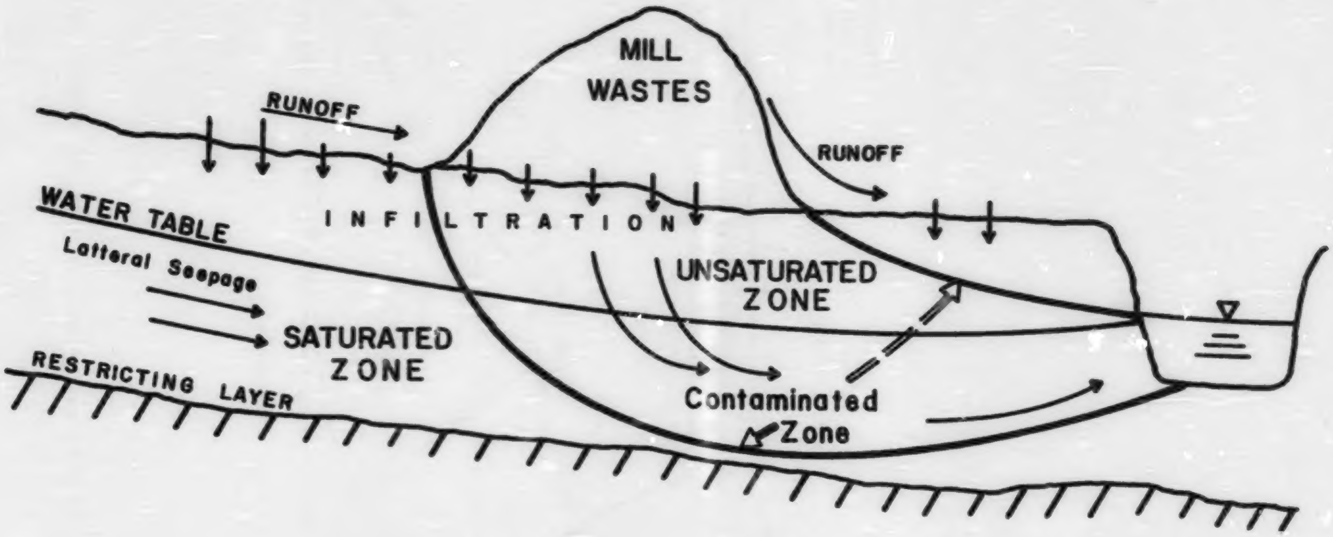
MILL
WASTES
RUNOFF
RUNOFF
WATER TABLE
INFILTRATION
Latteral Seepage
UNSATURATED ZONE
SATURATED ZONE
Contaminated Zone
RESTRICTING LAYER

Figure 35. Lateral movement of pollutants from waste heaps to surface water.

may repel water and thus reduce the problem of seepage through the pile and into the soil underneath. This would increase the problem of erosion and movement of the material via surface runoff, however. A permeable base will tend to reduce the amount of surface runoff, especially if water infiltrates through the pile easily.

Determination of waste transport from heaps by surface runoff can be made by observations and by sampling of water and sediment. Heaps can be observed for development of gullies or movement of material toward the base. Surface soil samples should be taken upslope and downslope of the heap and analyzed for variation in heavy metal concentration. If there is a distinct gully or channel near the heap which has periodic flow, water samples should be taken. Sediment samples from the channel's bed should be taken with distance from the heaps. Water samples should be taken from any ponded area that may include drainage from the waste site. Nearby streams should be sampled upstream and downstream of the disposal site during base flow and during stormwater runoff events. Sampling frequency will depend upon whether automated samplers are used, but some samples should be taken during the first hour of a rainfall runoff event when erosion potential is probably highest.

Some laboratory experiments may help if modeling is desired. Small heaps of wet or dry wastes with various slopes and slope lengths could be exposed to simulated rainfall to determine erosion potential and changes in the waste pile surface characteristics. However, the extent of the environmental pollution problem due to surface runoff needs to be quantified before developing elaborate experiments in the laboratory.

Under well-drained conditions of a heap with a permeable base, an aerobic environment would prevail and many soil fungi, actinomycetes, and bacteria, may actively invade the dust metals at the heap-soil surface. Soil microorganisms may assimilate and utilize some of the metals. In acid soils at pH below 6.5, metals like sodium, calcium, magnesium, arsenic, rubidium, antimony, and strontium may become soluble and may possibly contribute to pollution of surface waters. At pH above 6.5, little groundwater pollution is expected. Wetting and drying of the pile may lead to oxidation of iron, aluminum, and manganese in the steel mill dust to form ferric oxide, aluminum oxide, and manganese dioxide. These sesquioxides can adsorb other heavy metals but there is very little likelihood of their movement unless severe erosion of heap and soil takes place. Loss of organic matter by intense decomposition may create circumstances where copper is lost in drain waters and may ultimately contaminate the streams with copper. Electric process steel mill wastes possess high molybdenum and mercury which require special management practices to prevent the pollution of surface and groundwater. Molybdenum presents a pollution problem under alkaline conditions when it is most soluble and mobile, whereas, mercury becomes mobilized by the formation of methyl mercury.

Various factors affecting aerobic transformations and transport of metal ions are: temperature; rainfall intensity; soil-metal heap contact area; composition and characteristics of metal heap; soil characteristics and pH; redox conditions, fluctuations, and associated transformations of metal ions in metal-heap-soil systems; and biological and biochemical forces of weathering that produce organic substances that dissolve, chelate, or stabilize metals in residue heaps.

The present distribution of pollutant materials can be obtained by taking soil samples at various depths both close to and laterally removed from the heap. Care should be taken so as not to contaminate samples with waste materials near the surface. The device described by Terry, et al. for taking soil samples from specific zones would appear suitable for this purpose.[35] It may require modification for deep sampling. Sampling should be concentrated in the direction of lateral groundwater movement which could possibly be determined from surrounding wells, streams, etc.

If possible, both water and soil solids should be analyzed at each sampling depth. This would indicate the proportion of material that is tied up on the soil solids as well as that which is mobile.

Groundwater should be sampled on a continuing basis from observation wells placed in the vicinity of the heap. Existing wells in the area should be sampled and analyzed for the various pollutants.

The most critical case would be a shallow water table (10-30 ft) with permeable soils such as sands or sandy loams. These sites might be found in the Great Lakes area. On the other hand, pollutant concentration would tend to be higher in tighter soils, and the zone of contamination would move more slowly. The hazard here would be movement of the contaminated zone over several decades and its subsequent effect on water supplies.

The long-term fate of the heaped waste materials may also have implications so far as groundwater is concerned. The following case demonstrating this point is cited.[30]

> "A unique case of groundwater contamination by chromium occurred in the city of Grandville (Michigan) west of Grand Rapids. In this incident, the city drilled a public supply well in the glacial-drift deposits along the Grand River. To protect the well from flooding during periods of high water, the casing was extended several feet into the air and the land surface was raised by filling with sand and gravel. In time, chromium was detected in the water. This resulted in considerable consternation, since there was no apparent source of chromium contamination in the vicinity. Investigation by the Grandville Superintendent of Water revealed that the sand and gravel fill used to raise the land surface at the well was taken from a former dumping grounds for electroplating wastes! The river was in flood stage shortly before the contamination appeared. Water from the river obviously had leached the chromium from the fill and carried it into the aquifer."

7.3.2 Gullies or Natural Depressions

This case may be most hazardous of all so far as water pollution is concerned because water from a larger watershed area passes over or through the waste with the potential to both erode the actual material and to transport soluble species downstream and through the soil.

7.3.2.1 Mill Waste Placed in Gullies or Natural Depressions with No Retention Structure--

This case has maximum potential for surface runoff. Contamination can occur from both erosion of solid material and runoff water contaminated from having gone through filled waste material. Again, there is subsurface seepage both laterally and vertically as described above for above-ground heaps. Both permeable and impermeable bases apply. A similar sampling procedure as described above for groundwater and for soil can be used for this case.

In this case, there is a large amount of surface runoff and erosion because the material has been located in a natural drainage channel. Rainfall events would be the critical time for sampling water upstream and downstream. Between rainfall events, sediment should be sampled downslope of the waste pile.

7.3.2.2 Mill Waste Placed in Gullies or Natural Depressions with a Retention Structure--

Runoff from wastes in gullies is an obvious problem so a dam may have been put in the gully to prevent direct runoff (Figure 36). Also the mill waste itself may have redistributed to form a dam which results in the same situation. In this case the downard seepage would be maximized. Water would be ponded behind the dam or retention facility and slowly move either laterally or vertically from the heap. The increased infiltration under the wastes could cause a localized rise in the water table and lateral movement of the contaminated water. Where this situation already exists, drilling and sampling vertically under or close to the waste would be the best way of determining potential hazard to groundwater as discussed above for heaps. If the disposal site is located on a hilly area or if there are wells or natural drains such as streams or canals in the area, there may be considerable lateral water movement in the saturated zone.

For this case, investigations should be concentrated on groundwater and lateral seepage rather than runoff. Runoff would occur only from overflow from large rainfall events, or from seepage through the dam. The overflow would be more critical.

A trickle tube placed near the top of the dam would increase the potential for runoff, but there would still be the same problem with subsurface movement. In this case, one must determine the effects of both subsurface movement and surface runoff. Samples should be taken at the source of the overflow and downstream whenever overflow occurs.

A drain placed in the lower part of the retention structure would reduce surface water movement because water would no longer stand behind the dam. However, the concentration of solutes in the runoff water would be increased since all of this water would have filtered through the waste heap. Erosion

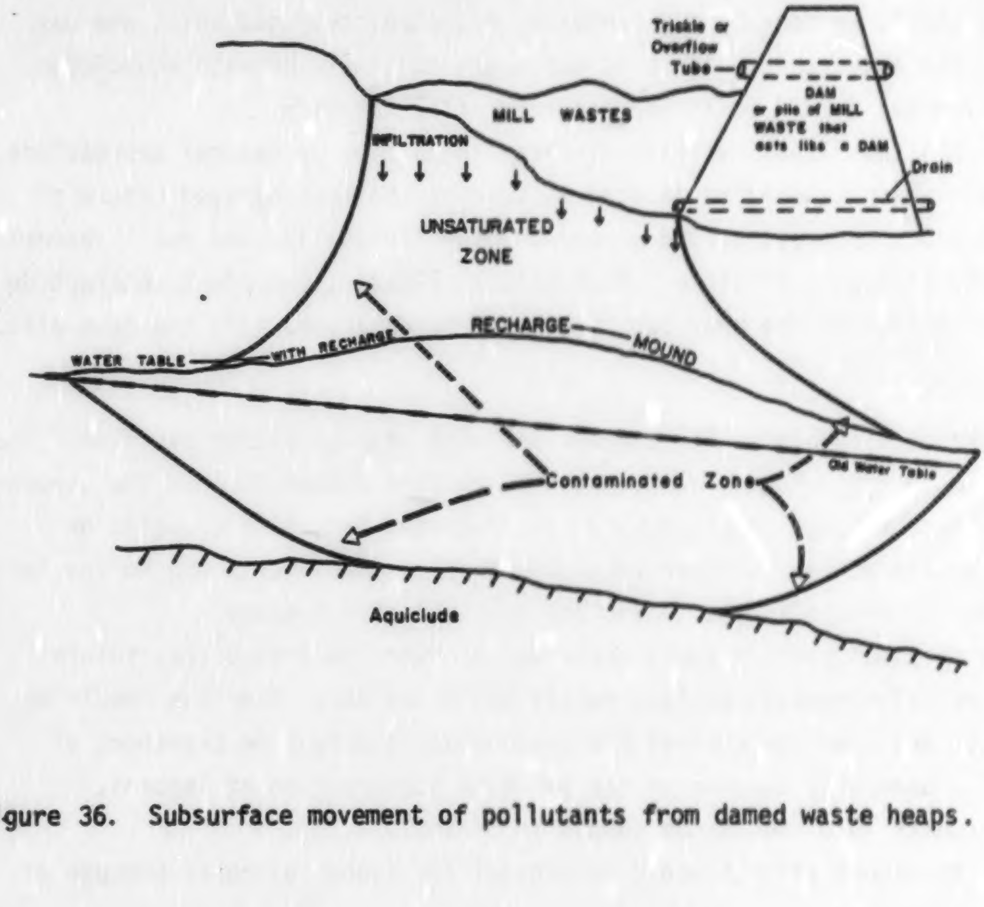
Trickle or
Overflow
Tube
DAM
or pile of MILL
WASTE that
acts like a DAM
Drain
MILL WASTES
INFILTRATION
UNSATURATED
ZONE
RECHARGE
MOUND
WATER TABLE
WITH RECHARGE
Old Water Table
Contaminated Zone
Aquiclude

Figure 36. Subsurface movement of pollutants from damed waste heaps.

of the particles would be reduced since water velocities are reduced, but there still would be more subsurface movement than with heaps because water could pond behind the structure for short periods of time.

7.3.2.3 Determination of Effects --

Sampling of soil and water should be as discussed for heaps above. More emphasis is placed on subsurface sampling than with heap disposal. Drilling holes for deep sampling should be done carefully and should not penetrate restrictive (very slowly permeable) layers which are called aquacludes. Drilling through an aquaclude for sampling purposes might provide a path for the movement of pollutant-laden waters below the restrictive layer. Drilling should be done by a groundwater hydrologist or geologist who can identify the aquacludes. If it is necessary to sample beneath aquacludes, the drill holes should be filled securely after sampling.

For all the cases involving disposal in gullies or natural depressions, airborne transport would be reduced because of the less exposed nature of the dust piles. However, wind movement occurs in gullies and small channels, hence wind pickup is possible. The soil, soil-water, and plant interaction would be similar to the previous case, once material has left the dust pile.

7.3.3 Lagoons

The main problems with lagoons are with seepage and/or overflow. The relative magnitude of each component will be case dependent. If the lagoon is not lined, seepage to groundwater aquifers and laterally to wells or natural drains would be higher than any other case. This is due to the fact that water is always in the lagoon and available for seepage.

The critical periods would occur during overflow from excess rainfall. Seepage may also produce surface runoff below the dam. Overflow should be sampled at the overflow channel and downstream to determine transport of material. Generally because of the pit-like construction of lagoons, surface runoff into the lagoon should be minimal.

Air transport effects would be minimal for lagoon disposal because of the constant water cover on the furnace dust.

In the inundated environment around the metallic waste in the bottom of the lagoon, anaerobic conditions will be associated with the reduction of metal ions and compounds. The anaerobic bacterial population would predominate in the total biomass of the system. The reductive reactions and formation of organic acids in the submerged solids would solubilize metals which would then be more subject to leaching as reduced metal ion species or soluble chelates. The soluble constituents of metal dust would diffuse in the direction of the activity gradient of the metal species and move as solute with water to lower horizons and possible to groundwater.

Under flooded conditions, fermentation of organic materials results in the initial production of organic acids which is followed by formation of bicarbonate, carbonate, sulfides, and other reduced states of metal ions. As a consequence, at first there is appreciable mobilization of zinc, manganese, iron, lead, nickel, copper, cobalt, vanadium, and magnesium but later on some of the metal ions precipitate as carbonates (lead) and as sulfides (iron, mercury, copper, tin, lead, nickel, cadmium, cobalt, manganese) in the advanced stage of anaerobiosis. Some metal ions, e.g., copper, nickel, etc., do irreversibly complex with organics. Copper can chelate with both -COOH and -SH groups. Under flooded lagoon situations, no mobilization of chromium, titanium, and molybdenum is expected.

The extent of pollutant movement from the lagoon can be measured by sampling soil and water phases as discussed above. Drill holes for determining vertical pollutant movement should be made close to but not in the lagoon. Again, care should be exercised in deep sampling because pumping of wells near a lagoon may speed up the lateral movement of contaminated waters. In humid regions, lagoons may overflow especially if they are in tight soils because rainfall often exceeds evaporation. For these cases, runoff must be considered.

7.3.4 Landfill

For a lined landfill with surface water excluded by diversions or because of location on high ground, there should be no soil-water movement problems. Again, one should check soil and water samples near such landfills as a possible best technology.

Surface water should be diverted from inclined landfills located on high ground. No interception of subsurface water would be anticipated since the only water movement is due to rainfall striking the surface of the heap. There could thus be both deep and lateral seepage which is essentially the same as the lagoon discussed above but with less water to move out. Such landfills present no problem with surface runoff unless seepage can produce surface runoff somewhere downslope from the landfill site.

Air transport could exist if daily covering of filled dust with a soil layer was not practiced. Operation with soil covering is similar to standard sanitary landfill practices presently used for municipal refuse.

Where the unlined landfill is located in the path of natural subsurface flow, water could move through the waste and carry pollutants to receiving streams or to groundwater recharge areas. Here there is a need for monitoring wells downstream from the landfill. This is essentially a special case of the pile insofar as subsurface water is concerned but potentially more of a problem because the landfill can intercept subsurface flow thus presenting an opportunity for increased dispersion.

SECTION 8

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APPENDIX A

SPECIFIC GRAVITY DETERMINATIONS

RESULTS

Specific gravities were estimated for the 18 samples provided. The results are tabulated in Table A-1.

PROCEDURE

Each sample was split in a Sepor sample splitter, oven dried, and then allowed to return to room temperature in a dessicator. Splits were then weighed and placed in 50 ml cylinders. Water was added to each cylinder to the 40 ml line using a graduated 50 ml burette. Water displaced by the sample was 40 ml minus water introduced from the burette. Specific gravity was then estimated as weight of sample split divided by weight of water displaced.

CHECKS AND CAUTIONS

Entrapment of air by the fine material in the cylinder was minimized by introducing 10 ml of water initially, then slowly adding the sample material. The slurry was then briefly vibrated before bringing the water level to the 40 ml mark.

Water used was demineralized, and a check was run on its specific gravity (Table A-1). The difference between expected and observed values are within the error limits expected by the technique (1 burette drop = 0.06 gm).

Tests of the technique (Table A-1) were made using the mineral quartz (s.g. = 2.65), both as a single crystal (sample A) and as a very fine sand/silt (sample B). In both cases, error for the technique is about 1 percent.

Two uncontrolled sources of variation could effect the results. Composition could vary with grain size and small bubble inclusions within grains could change proportion with grain size. The specific gravity estimates, therefore, are averages for the bulk sample.

TABLE A-I. SPECIFIC GRAVITY ESTIMATES

Sample No.	Wt. of Sample Split (gm)	Water Displaced (ml)	Wt. Water** (gm/ml)	Specific Gravity Estimate
1	12.421	3.05	1.000	4.07
2	14.121	3.93	"	3.59
3	7.025	1.35	"	5.20
4	14.498	3.76	"	3.86
5	12.892	2.93	"	4.40
6	6.376	1.57	1.000	4.06
7	11.394	2.70	"	4.22
8	12.100	3.10	"	3.90
9	13.649	3.36	"	4.06
10	17.826	4.16	"	4.29
11	8.499	1.79	1.000	4.75
12	13.178	3.20	"	4.12
13	13.217	2.89	"	4.57
14	14.682	3.68	"	3.99
15	11.752	2.77	"	4.24
16	11.541	3.06	1.000	3.77
17	11.122	2.70	"	4.12
18	10.915	2.56	"	4.26
(Qtz. sand)				
A.	23.825	8.89	1.000	2.68*
B.	29.791	11.32	"	2.63*
(Water Used):	40.146 gms;	40.33 ml vol;	S.G.= 0.996**	

*Quartz = 2.65, expr. error ∿1%

**Within margin of burette error, assumed 1.0 subsequently

APPENDIX B

PARTICLE SIZE ANALYSIS

RESULTS

Particle size distributions for the 18 samples provided were presented in Table 9. Table values are in weight percentage by size classes. Size classes are divided on the phi particle scale (phi = $-\log_2$ mm), and equivalent micron size ranges are given. Particles coarser than 4 phi were determined by wet sieving; those finer by pipette analysis where the table is completed. For those samples not analyzed when the study was terminated, the finer than 4 phi row contains a double-headed arrow. The arrow shows the sedimentation size range based upon visual sedimentation.

PROCEDURES

Each sample was split on a Sepor sample splitter, its dry weight determined, and placed to soak overnight in a covered beaker.

The splits were then washed through a No. 230 U. S. Standard Sieve (4 phi size boundary). Gentle rubbing of the sieve fraction often was necessary to break apart aggregates. The fraction passing the sieve was transferred to a 1000 ml cylinder for subsiquent pipette anlaysis The fraction collected on the screen was oven dried, cooled, and weighed. This computed percentage is in column 1 of Table 9.

The finer than 4 phi fraction of each split was transferred to a 1000 ml cylinder. Sodium oxilate was added to each cylinder as a peptizer. The cylinders then were allowed to sit overnight and come to equilibrium with controlled room temperature (22°C). The following morning, the fractions were analyzed by standard pipette analysis, based upon Stokes' law of settling velocities of spheres through a water column. The resultant summary percentage values are in Table 9. Details of the pipette procedure follows.

Pipette analysis was discontinued after half of the samples had been run because of flocculation problems. The effective grain size range of the finer fraction for the remaining samples was estimated roughly by stirring the 1000 ml cylinder mixtures, then timing how long before a marked card could be seen through the water column (about 10 cm depth). These size ranges are depicted in Table 9 by double headed arrows.

REPLICATIONS

Three samples were randomly selected for replicate analysis, subject to the limitation that one be from each of the three groupings provided (OH, Electric, BOF). Sieve replications were good in all samples; pipette is good in No. 7. Pipette discrepancies in No. 15 may reflect incomplete disaggregation, as the sample contained hard clumps when sieving which were difficult to break down.

PIPETTE ANALYSIS

Pipette analysis is a standard sedimentation technique for analysis of grains finer than sand size. Its major area of utilization is in soil spheres through a water column:

$$V = 2/9 \cdot (d_1 - d_2)\, gr^2/\eta$$

where: V = settling velocity (cm/sec)
d_1 = particle density (gm/cc)
d_2 = fluid density (assumed 1.0 gm/cc)
g = gravity (assumed 980 cm/sec^2)
r = particle radius (cm)
η = fluid viscosity (assumed 0.01 poise)

Since velocity also equals distance (or depth) divided by time, knowing the particle density one can solve for the time necessary for a particle of a given diameter to have fallen through a given distance of water column.

Utilization of this law in size analysis typically involves the following steps:

a. the material is thoroughly mixed through a column of water of known volume (1000 ml in this case). The instant external mixing ceases is time "zero", and it is assumed the sediment at this instant is homogeneously dispersed through the water column;

b. at a predetermined time a 20 ml pipette is inserted to a predetermined depth and a sample extracted. This sample can contain only grains of a diameter less than the calculated size;

c. the 20 ml extraction sample is placed in a beaker, and the water evaporated off;

d. the weight of the sediment contained in the 20 ml extraction is determined, and corrected for peptizer present. Since the sample is only a fraction of the suspended volume (20 ml of 1000 ml), it must be proportioned up (times 50 in this case). The result is the weight of material finer than a given size in the suspension;

e. weight between selected size limits is determined by subtracting the "finer than" weight of the lower boundary from that of the upper boundary. Weight percentage in each size class may then be calculated.

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APPENDIX C

SPARK SOURCE MASS SPECTROMETRY DETERMINATIONS

SAMPLE PREPARATION

The samples, as received, varied widely in their gross appearance and visual homogeneity. Representative portions of each sample were taken and dried to constant weight, then ground in a mixing mill to improve the homogeneity of the material and to afford better mixing with the graphite support material. One sample, number 15, showed a significant weight loss on drying.

Five milligrams of the dried sample were mixed with fifty milligrams of graphite, the erbium internal standard added; and the resultant mixture evaporated to dryness under an infrared lamp. The dried mixture was shaken further in a mixing mill to achieve homogeneity. The electrodes were then compacted.

Notice was taken of some segregation of sample and graphite on shaking in the mixing mill if the sample had not been ground before mixing. Evaluation of several mixing methods was performed, and it was found that all that incorporated a pre-grinding of the sample material were satisfactory (judging from the reproducibility of the results).

ANALYSIS

The usual graded series of exposure were taken (10^{-4} - 300 nC, in steps of a factor of 3) by photoplate. One photoplate was exposed per sample, due to the time limitations specified in the request for analysis and also due to a scarcity in the supply of photoplates. The exception to this is sample no. 1, on which the mixing technique/homogeneity study was performed on four sample electrode sets.

CONCLUSIONS

The results reported here of the analysis of 18 samples by SSMS yielded the normal precision that can be expected from SMSS photoplate analysis. Noting the usual caveat concerning the sample homogeneity requirements of SSMS, the results should be as good as the sampling.

APPENDIX D

SOLUBILIZATION TEST PROCEDURE

PROCEDURE

Eighteen steelmaking furnace residues were subjected to solubilization by contacting 125 grams of sample with 250 milliliters of deionized water. The mixture was shaken for 48 hours and allowed to stand for 16 hours to facilitate solid/liquid separation. A portion of the solute was drawn-off and analyzed. The pH of the solutes were also measured.

The amount of solute drawn-off was replaced with fresh deionized water, and the process was repeated. A total of ten contact periods was used.

CONCENTRATION CALCULATIONS

With only a portion of the solute drawn off at each contact, a certain amount of "residual" concentration would be left in the liquid. This residual would affect the concentration of the successive contacts. Thus, the residual must be accounted for in the calculation of subsequent concentrations. This is done by the following:

$$\left(\frac{250 - \text{Quantity Removed}}{250}\right)(\text{Concentration}) = \text{Residual.}$$

A plus and minus 15 percent of the residuals was also calculated to provide an error range. The concentration reported was then a difference between the analysis result and the ± 15 percent range.